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Ennis, Wesley D.; Hufft, John C.

Rensselaer Polytechnic Institute, Troy, N.Y.

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THESIS
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AN INVESTIGATION OF THE EFFECT OF IONIC SUBSTITUTION ON THE ATTERBERG PLASTICITY CONSTANTS FOR CERTAIN CLAY MINERALS

WESLEY D. ENNIS AND
JOHN C. HUFFT

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by
WESLEY D. ENNIS
Lieut. (jg), CEC,USN

and

JOHN C. HUFFT
Lieut. (jg), CEC,USN

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15615

TABLE OF CONTENTS

Page

Introduction 1

Theory 7

Apparatus 24

Preparation of Samples 26

Testing 43

Results and Conclusions 53

  Recommended Procedure for Preparation of Homoionic Clays 56

  Tabulated Results 61

Appendix A 62

  Atterberg Constants Determination Data

Appendix B 82

  Potentiometric Titration Curves

Appendix C 87

  Flow Curves

Bibliography 98

Supplements 100

INTRODUCTION

INTRODUCTION

It has long been known that the clay fraction has a great effect upon the properties of a soil, both agricultural and engineering. This influence is due to the surface activity, the mineralogical composition, and the plate-like shape of clay particles. Because of this great effect it is mandatory that extensive study be made of the clay fraction in order to further the understanding of clay-bearing natural soils.

Clay may be defined as a crystalline, hydrated alumino-silicate formed by the hydro-decomposition of feldspars or similar silicates. Two general groups of clay minerals have been recognized: the kaolin group with a 1:1 type of crystal lattice; and the montmorillonite group with a 2:1 type of crystal lattice (1). Though both groups are clays, there are marked differences in the properties exhibited by each. The kaolin group characteristically show little tendency toward hydration, do not swell upon wetting, and have a low base exchange (cation adsorption) capacity. The montmorillonite group show a great tendency to hydrate, expand tremendously upon wetting, and have a relatively high base exchange capacity.

It has been further determined experimentally that the properties of the clay itself are dependent to some extent upon the cation which is attached to the clay particle. These cations may be supplied in many ways: sodium chloride in sea water provides the sodium cations which are found in marine clays; a farmer supplies calcium cations when he spreads lime over his land, and that is precisely why he does so for the calcium ion improves the agricultural properties of his soil.

Numerous investigations have been conducted which reflect all of the above facts, but so far very little of the information gathered has been of direct value in engineering. The ceramic industries, colloidal chemists, and agriculturalists have gathered many data. The engineer finds this information useful, but seldom of immediate application, and so there remains much to be done, especially of a quantitative nature.

One of the qualities of natural soils which is affected by all of the above factors is plasticity. This property is exhibited by nearly all soils to some extent when wet, and in most cases it is due to the clay fraction. Plasticity has been defined by Mellor as "the property which enables a clay to change its shape without cracking when it is subjected to a deforming stress."

In 1911 Atterberg (2) (3) proposed two simple tests for defining the plastic properties of soils. These tests have come to be known as "liquid limit" and "plastic limit" determinations. The liquid limit is that water content at which the soil is practically liquid, but has a small, arbitrarily chosen shearing strength. The plastic limit is the smallest water content at which a soil is plastic. The difference between the plastic limit and the liquid limit is the water content range through which the soil exhibits plasticity and is known as the "plasticity index". Atterberg's method of determining the plastic limit is to roll out samples of the soil, slowly decreasing the water content, until the soil just crumbles when a thread one eighth inch in diameter is obtained. This test, though seemingly crude, gives consistent results and is the method used at the present for obtaining the plastic limit. The method proposed by Atterberg for liquid limit determination was susceptible to personal error, and a more satisfactory method was proposed in 1932 by A. Casagrande (4). The apparatus designed by Casagrande gives consistent results and is now used exclusively for liquid limit tests.

The Atterberg plasticity tests have become widely known, and are used by many soil investigators. Admittedly empirical in nature, they nevertheless are

valuable in giving a "feel" for the character of soils. Perhaps the most specific use of these tests is in the Casagrande system of soil identification and classification for airfield projects. This system involves visual inspection, grain-size analysis, and Atterberg tests, and provides rapid, easy, and usually dependable results. Some state highway departments have specifications relative to the allowable plasticity index for certain subgrades. All in all, it may be said that the Atterberg tests are widely known and extensively used by soils engineers.

With the above facts in mind, it was decided to determine the Atterberg plasticity constants of three important clay minerals with various cations attached. Kaolin from Dry Branch, Georgia, was selected as typical of the 1:1 lattice clay mineral. Bentonite from Rock River, Wyoming, was chosen as typical of the 2:1 lattice clay mineral (montmorillonite group). A third clay mineral called Illite was also tested. Illite has a 2:1 crystal lattice, but does not show the extreme characteristics of the montmorillonite group. The sample tested was Illite Bond Clay from Joliet, Illinois.

Having selected the clay minerals to be investigated, it was next necessary to decide which cations should be placed on the clays. Hydrogen, calcium, sodium, and potassium cations are found

extensively in natural soils, and are very important in determining the properties of those soils. These cations were thus selected.

The investigation then was defined, and divided itself into two parts: 1) preparation of the clays to be tested - hydrogen kaolin, calcium kaolin, sodium illite, potassium bentonite, etc.; and 2) determination of the Atterberg plasticity constants of these samples.

THEORY

THEORY

Water Film Theory

Probably the leading and certainly the most universally accepted theory accounting for soil plasticity is the water-film theory. Soil plasticity has been defined as that condition of a soil-moisture mixture in which it can be deformed without rupture by an applied force and will not return to its original shape. The soil will remain in its deformed shape when the force is removed. Plastic soils to which such a force is applied are said to be plastically flowing when deformation occurs. This soil condition is similar to the state of strain found in steel at stresses above the yield point. (i.e. stress is not proportional to strain but rather a constant and continuous strain occurs for a given applied stress.)

In soils, water is the basis of this plasticity. Without water the clay soils are hard and exhibit pronounced coherence. Soils with too much water are fluid and viscous. These fluid soils will deform without benefit of an applied force and hence show no plasticity. Somewhere between these two extremes of soil-moisture lies the range of plasticity.

Plasticity and plastic flow are visible manifestations of the physical property of clay soils known as cohesion.

Cohesion has been defined for wet soils as the attraction between the molecules of the liquid phase (water) and adjacent clay particles. The above definition simply means that the water molecules "bridge" the gap between clay particles. These water bridges are, in reality, water films made up of oriented water molecules.

Water molecules are dipole in nature (i.e. they have a positive charge on one end and a negative charge on the other.) These molecules are thought to have a length greater than the width. These properties of water molecules enable them to be oriented in the presence of an electrical field.

The existence of an electrical double layer around clay particles has been known for some time. (Helmholtz double layer) The inner layer is composed of unsatisfied valences from the atoms in the clay crystal structure. This negative charge around the clay particle makes it very effective in orienting the water dipoles. The result is a close packing of the water molecules near the surface of the clay particles. This packed condition imparts different properties to the water than ordinary free water possesses. The water thus held has a higher density, lower freezing point, and capable of greater tensions to mention a few physical properties. As the thickness of the water film increases, the above properties of the outer film water more nearly approach those of free water.

The attraction of the outer water to the clay particle naturally decreases as the film grows thicker due to the greater distance between the two bodies. It is the film tension of oriented water molecules, which imparts cohesion to the soil by bridging the gaps between the particles. These water molecules, however, are not the only factor which aids in bridging these gaps as will be shown later.

The picture of soil plasticity can now be clearly seen. As water is added to a dry powdered clay soil, the water is immediately drawn to the surface of the clay particles by the forces explained above. The first small amount of water merely makes the soil crumbly and friable. Friability characterizes the ease of crumbling of soil. It is the moisture range over which the clay particles are held together, in part, by the oriented water molecules. (5) Agriculturists know this state of soil moisture to be that at which optimum tillage occurs.

Further addition of water coats all the surface of the clay particles with water. There is no longer grain to grain contact, but instead the contact runs from grain to water to water to grain. The water content at which each clay particle receives just enough water to coat it completely and allow it to attach itself to a neighboring particle, is a very important condition of soil and moisture. It is here that we have Atterberg's

Plastic Limit (sometimes called lower plastic limit). It is at this moisture content that the bridging first occurs completely and it is also at this point that it occurs the most tenaciously. Since the water molecules are closely packed and, therefore, have high tension, the water will exhibit shearing strength. In addition, it is at this condition of soil and moisture that the mixture enters the range of plasticity. Consequently, the plastic limit is of extreme importance in the study of clay soils.

If the addition of water to the clay is continued, the films around the particles will become thicker. The films still exhibit tension at the points of contact but the tension has been reduced below that for plastic limit. The water dipoles are still oriented around the particle, but this additional water is not as strongly held. The reason is that the water molecules are now further from the negative Helmholtz inner layer because of the thickness of the film. As more water is added, the films grow thicker, and finally a point is reached where the orienting force is zero due to the very thick water film. The dipole molecules are now no longer held to the outer fringe of the film, and the film has reached maximum thickness. As would be supposed, the water on the outside of this film now has the properties of free water, i.e., no tension. The soil-water mixture now behaves essentially as a fluid exhibiting no shear strength. The mixture flows

without an applied force and, therefore, cannot be considered plastic. This type of flow is viscous flow. The upper end of the zone of plasticity has now been reached. This upper end point was called by Atterberg the Liquid Limit (sometimes referred to as the upper plastic limit). The reason for the name is obvious.

The difference in moisture content of the clay between the liquid and plastic limit is known as the plastic index. This index is a measure of the range of water contents over which the soil is plastic. Soils with high indices will hold a large quantity of water and still exhibit shearing strength, while soils with low indices are likely to liquefy upon the addition of a small amount of water. Soils with high indices, however, are likely to settle large amounts even though they have appreciable shearing strength.

A brief mention will now be made of the clay particles themselves. All clays are characteristically composed of flat particles. This physical property is due to the sheet-like structure of the clay crystals. The flatness imparts different properties to a clay-water mixture than a round particle-water mixture would have. It takes more water to completely coat each of these particles than for a spherical particle. The Atterberg Limits are, consequently, higher for clay soils. When clay systems are subjected to a deforming force, these particles slide over each other, thereby imparting

different plastic properties to the clay-water mixture.

The Atterberg Limits have additional practical value to those previously mentioned. Soils with a high liquid limit should either contain a large quantity of excessively fine grained fractions or be rich in plate-like particles. The reason for this statement is now obvious. Large quantities of small particles indicates a large quantity of water is required to completely satisfy the film requirements of these particles. Lastly, soils having both a high liquid limit and a low plastic index are in a finely divided state. If the plastic number is high, the soil contains an abundance of plate-like particles.

Factors Affecting Atterberg Limits

Investigators have determined that Atterberg Limits are not constant for a given soil but vary with the per cent of clay (5 micron size and below), the silica-sesquioxide ratio, and the quantity of organic matter present. Thus, the same basic type of clay may have different Atterberg Limits depending upon the above factors.

The percent of clay has an effect on the plastic limit, the liquid limit, and the plastic index. If the soil has a high percentage of small particles (5 micron and below), a large quantity of water is needed to completely coat each particle and thus bring the soil up to the plastic limit. Consequently, the plastic limit is raised. In a like manner, a large quantity of water is required to completely satisfy the film forces and bring the clay-water mixture to the liquid limit. As a result, both the liquid limit and plastic index are also raised. Therefore, the effect of clay upon Atterberg Limits is to raise (or lower) all the constants depending upon the quantity of clay present. (2,3,6,)

L. D. Baver (7) has shown the effect of the silica-sesquioxide ratio upon the Atterberg Limits. In the referred paper it was shown that the physico-

chemical properties of the colloid clay vary with this ratio. The adsorptive capacity of the surface of the colloid for water or various ions decreases as this ratio becomes lower. Since adsorption and consequently the amount of water required to create the films around the particles is small, the moisture content at which plasticity begins is low. Once the film has been formed, the amount of water necessary to reach the liquid limit is dependent upon the clay content. As the clay content was considered constant for all soils considered in this investigation, the net result of a low silica-sesquioxide ratio is to lower the plastic limit, lower the liquid limit, but leave the plastic index unchanged.

The quantity of organic matter present also has a decided influence on the Atterberg constants. Organic matter has a strong attractive force for water. This attraction is so strong that it robs the clay particles of the moisture. (8) Thus, water added to soils containing organic matter is adsorbed first by the organic matter. When this material becomes satisfied, the clay commences adsorbing the water. As a result organic matter raises both the plastic limit and the liquid limit. The plastic index remains unchanged for the same reason that it remained unchanged in Baver's investigation of the effect of the silica-sesquioxide ratio.

The last factor affecting the Atterberg Limits is cation saturation, an investigation of which is the purpose of this thesis. In the discussion of the water film theory it was pointed out that the water films were not the only forces bridging the gaps between the clay particles. Russell (5) was one of the first to suggest that exchangeable cations assisted in holding clay particles together. The following is quoted directly from his paper, as it amply explains the function of the cation in soil structure.

"Each particle is surrounded by an electrical double layer, the outer one being diffuse and consisting of cations, while the inner layer consists of negative charges presumably anchored on the surface of the particle. The cations in the diffuse layer move about in the water in the same way as they do around a complex anion, as pictured in the Debye-Huckel theory of strong electrolytes. Since the water molecules possesses a dipole moment, they tend to be oriented along the lines of electric force radiating from each ion in the diffuse layer and from each free charge on the surface of the clay particle. Every cation and particle is thus surrounded by an envelope of oriented water molecules, and the orientation manifests itself as an apparent adsorption or immobilization of water by the clay.

"A clay particle in a dilute suspension can, therefore, be pictured as consisting of a central core surrounded by a surface carrying a negative charge. Around each negative charge is an envelope of water molecules which are more oriented the nearer they lie to the charge. Outside this surface are the cations, also possessing envelopes of oriented water molecules. Some cations are so close to a negative charge on the surface of the clay particle that the two water envelopes belonging to these charges overlap and the water molecules in this region are oriented in their joint field. This orientation is very strong since the negative end of the water dipole is attracted to the cation and the positive end to the particle's surface.

"As the water is removed, the deflocculated clay suspension becomes more and more concentrated, and an increasing proportion of the water molecules become oriented in the joint field of a positive and a negative charge. It is reasonable to assume that a certain number of cations will share their oriented envelopes with two clay particles. A linking system is thus set up consisting of; particle-oriented wetting molecule-cation-oriented wetting molecule-particle." This quotation amply explains the role of the cation in soil-moisture mixtures. These cations are supplied by salt solutions found in ground water. The effect

of various types of cations on the Atterberg Limits is shown in the discussion of the results of this investigation.

To broaden the above picture presented by Russell it should be realized that not only are cations adsorbed on the surface of clay particles, but in the 2:1 expanding lattice clays (montmorillonites) cations are also adsorbed between the sheets of the clay. Consequently, these clays are more influenced by adsorbed cations than the 1:1 lattice clays.

Jenny and Reitmeir have shown that not all cations have the same hydrated diameter. Their paper lists the ionic radius of the common cations frequently found in soil. Beside these are listed the hydrated size of the cations. The peculiarity noted in this paper is that the ions with the smallest ionic radius have the largest hydrated diameters. This simply means that all the ions do not hold or orient the same quantity of water. In addition, the smallest ions hold the largest amount of water. As a result, soils containing these ions in the outer Helmholtz layer will have varying physical properties due to the varying quantity of water adsorbed by these ions. Therefore, the Atterberg Limits are also affected by adsorbed ions.

Base Exchange

Although a study of base exchange in natural clay soils is not the purpose of this paper, it is necessary to mention this subject as the ultimate purpose of this investigation could not be realized without a consideration of it.

Base exchange was recognized as early as 1850 by Thomas Way in his classical work "The Power of Soils to Absorb Manure." Briefly, base exchange for clays is the substitution of a new cation for the cation already attached to the clay particle. Thus, a cation of one kind removes and takes the place of a different cation on the colloidal clay complex. It was noted in the discussion on factors affecting the Atterberg Limits that since cations are capable of being hydrated to varying degrees depending on type, they should logically have an effect on these important soil constants.

In 1932 Hans Jenny (12) conducted an extensive investigation on the mechanism of ionic exchange. Working with artificial and natural colloidal aluminum silicates Jenny made some very important discoveries. Among these were the following:

1. In all exchange reactions, a very pronounced lyotropic series was observed.
2. The strong adsorption and difficult release

of the hydrogen ion is easily understood by considering the strong chemical bonds between the adsorbed hydrogen ion and the oxygen and hydroxyl ions of the rigid crystal frame.

3. Ionic exchange affects the hydration of the colloid particles.

Jenny's first observation concerning a lyotropic series is very important. He found that for each aluminum silicate studied there was a definite order of release and an inverse order of adsorption for the cations considered. From the above he concluded that certain cations were held more tenaciously than others by the colloidal complex, thereby, giving an order or lyotropic series for the ease of adsorption or release of these cations. He found that, in general, the cations with the smallest ionic crystal radius were adsorbed with the most difficulty, and the most easily replaced. Jenny also pointed out that the smaller the ionic crystal radius, the greater was the hydrated diameter. To quote Jenny; "With the aid of the concept of hydration, the mechanism of ionic exchange is easily visualized. The strongly hydrated, large and voluminous Li-ion cannot come very close to the negative oxygen ion of the crystal lattice, since there are one or two water molecules between the colloidal particle and the adsorbed cation.

The forces of attraction are, therefore, weak because they vary inversly with the square of the distance between the electric charges, (Coulomb's Law). Adsorbed Li-ions are, therefore, easily replaced by the less hydrated and consequently smaller ions such as K, Rb, Cs which are very strongly attracted by the negative places in the crystal lattice."

Jenny, however, noted one outstanding exception to the above explanation for the existence of a lyotropic series. This exception was the place of the hydrogen ion in the series. On the basis of the small ionic size it would be logical to conclude that it would have the largest hydrated diameter. Therefore, it should be the easiest to replace and adsorbed with the most difficulty. However, such was not the case. Indeed Jenny found that the H ion was the best adsorbed of all ions and the most difficult to replace. To again quote Jenny;
"As to its release or exchangeability, the H-ion is the most difficult to replace; it sticks tenaciously to the colloid particle. Unless the electrolyte added is able to bind the liberated H-ion (as is the case with hydroxides), complete exchange with one salt treatment is hardly achievable. It seems, therefore, possible to trace the action of the H-ion back to the significant differences in the type of bonds between the cation and the anion. In the case of Li and Na where it is probable that at least one water

molecule stands between the O-- and the cation, attraction is weak and of an electrostatic type, while in the case of the H-ion, the forces are strong and seem to be a true chemical type."

In this investigation, H-clays (clays saturated with H-ions), were used as base clays. All replacement was made against these clays. This simply means that H-clays were prepared, and cations added to these clays to replace the H-ion. In this manner, Na, K, and Ca clays were prepared. This, at first, would seem to be the poorest method. However, the hydroxide of the above cations were used to effectively bind the released H-ion. Jenny specifically exempted hydroxide when speaking of the difficulty of the H-ion release.

There are various methods used for the preparation of base clays. Among the most popular are the ammonium acetate method and the hydrochloric acid method. Each has its own advantages. However, the use of hydrochloric acid to prepare base clays has two distinct advantages not found in other methods. These are the more complete replacements obtained by hydrogen and the rapidity with which other clays such as Na-clay, Ca-clay, etc., may be prepared. Jenny has shown that hydrogen (ion) is the best adsorbed of all ions. Therefore, the addition of the H-ion in

the form of hydrochloric acid will result in an H-clay with a high H-ion content. The H-ions give the clay distinctive acid properties when it is dispersed in water. This property leads to the second advantage of the hydrochloric acid method; that is, the rapidity of preparation of other homoionic clays. If a base such as NaOH is added to a dispersion of H-clay in water, a reaction between the two will take place in much the same manner as a reaction between a base and an acid. If the base is added to the clay in small uniform amounts and the pH measured after each addition, a potentiometric curve may be plotted for the pH against the base added. The rate of change of the pH is not uniform but changes slowly at first and then reaches a maximum as additions of base are continued. After the maximum is reached, the rate of change of the pH slows down. The milliequivalents of base added per 100 grams of clay conforming to the point of maximum rate of change of the pH is taken as the exchange value. This test is easily and rapidly conducted. If a quantity of any other base such as KOH is added in an amount conforming to the exchange value, a K-clay is produced, etc. In this manner K, Na, and Ca-clays were produced for testing.

APPARATUS

APPARATUS

A standard Casagrande liquid limit testing device was used for all liquid limit determinations. This device is completely described in A.S.T.M. Specifications.

The high speed mixer used in this investigation was a standard laboratory dispersion apparatus, similar in nature to a milk shake mixer. It is equipped with a stainless steel stirrer.

The variable speed mixer referred to was a small, variable speed electric motor driven mixer using a glass stirring rod.

The apparatus used for potentiometric titration consisted of a standard 50 ml. burette, the variable speed mixer, and a Beckman pH meter with calomel electrodes. A watch with a second hand was used in titration to equalize time intervals between addition of hydroxide and measurement of pH.

The vacuum filter apparatus consisted of ten 90 m.m. porcelain Buchner filter funnels, ten suction flasks, vacuum pump, and number 50 Whatman filter paper or equal.

The oven used to determine moisture contents was held at the standard 105° Centigrade.

PREPARATION OF SAMPLES

PREPARATION OF SAMPLES

General

The most difficult problem involved in the conduct of this investigation was the preparation of samples for testing. It was known that the soils as received were not pure specimens of the clay minerals Kaolinite, Illite, and Montmorillonite. It would have been possible to remove the impurities, at least a great portion of them, in order for the tests to be conducted on the pure clay minerals. However, the soils consisted primarily of the corresponding clay minerals (this may have been questionable in the case of the Illite Bond Clay) and, therefore, results obtained would be due principally to the clay minerals. Therefore, the soils were not purified. Instead, to achieve consistent and significant results, it was necessary to control the factors which could affect the Atterberg Constants. These previously named factors are amount of clay present, silica-sesquioxide ratio, organic matter, and cation present. It was necessary to assume that, for all practical purposes, the soil was uniform in composition, any one portion having the same clay content and silica-sesquioxide ratio as any other portion. There was no reason to doubt this assumption. The organic matter, if any, was removed by treatment with hydrogen peroxide. These factors having been controlled, any differences

in Atterberg Constants should have been due to the factor which was varied - the cation present.

As the work progressed, it was discovered that other considerations were involved, but it is believed that they also were controlled. The considerations will be mentioned later.

The Atterberg Constants of each soil as received had to serve as reference points for further tests, even though no information was available as to the cations present. Tests were conducted on each of the soils as received, after necessary grinding and sieving to meet A.S.T.M. specifications. Such determinations having been made, samples of the various homoionic clays were then prepared. (The term "homoionic", meaning one ion, is not literally correct. It is quite certain that the "homoionic" clays are not truly clays with only one type of ion attached. Winterkorn (10) and others, however, have used this term for clays subjected to the hydrochloric acid and hydroxide treatment used by the authors. In using the term "homoionic clay" the authors mean a clay which has been subjected to treatment to create a clay which has a given cation attached in a significant amount.)

It has been mentioned earlier that there are several ways to prepare homoionic soils. The authors had to have a rapid method of preparing relatively large samples, and it was desirable to have information

regarding the amount of exchange which had taken place. Leaching the soils with electrolytes to supply the cation would have been a slow process, many investigators having carried on the leaching for months. The only suitable method seemed to be the preparation of hydrogen clays (H-clays) by the addition of dilute hydrochloric acid, and then the necessary quantity of the hydroxide of the desired cation would be added to the H-clay. This method may be idealized as follows, using NaOH as an example:

$$(1)\quad \left.\begin{array}{c} \text{Na} \\ \text{K} \\ \text{Ca} \\ \text{and/or} \\ \text{any other cations} \\ \text{attached} \end{array}\right] \text{Clay} + \text{H Cl} \longrightarrow \text{H-clay} + \left.\begin{array}{l} \text{Na} \\ \text{K} \\ \text{Ca} \\ \text{Cations} \end{array}\right] \text{Cl}$$

The excess hydrochloric acid and the chlorides are then washed away leaving a pure H-clay.

(2) $\text{H-Clay} + \text{NaOH} \longrightarrow \text{Na-clay} + H_2O$

This latter expression reminds one of an acid-base chemical reaction, and that is precisely what it is. It is commonly accepted that H-clays have many of the properties of a weak acid, and it is this fact that makes the method preferable. Once an H-clay has been created, it is then necessary to add a specific amount of the desired hydroxide, and the corresponding homoionic clay is created. If just enough hydroxide is

added to complete reaction (2) above, it is seen that the products are the desired homoionic clay and water, the latter being easily removed if desired. It is necessary to know how much should be added in order to complete the reaction and yet prevent the presence of excess hydroxides which are not easily removed. This may be accomplished by conducting a potentiometric titration of the H-clay in a water suspension against the desired base, measuring the pH of the sol corresponding to added amounts of the hydroxide. A plot of pH versus amount of added hydroxide will give a typical acid-base reaction curve. Such curves are shown in Appendix B. The point at which the rate of change of pH is a maximum is the point at which the reaction is complete. (The pH of the completion of this acid-base reaction should of course be in the vicinity of 7, and as would be expected it turned out to be slightly above 7 in all cases.) Any further addition of hydroxide will naturally increase the pH, but the reaction has been completed. For strong acids and bases this point of completion is quite specific, and amenable to precise determination. With weak acids, which H-clays are, the rate of change of pH is never so spectacular as with stronger acids, but good results are obtainable if care is used in titration. Such potentiometric titration conducted on a small sample of H-clay will give the exchange capacity in milliequivalents per unit

weight of soil. This is the desired amount of base to be added, so to create a Na-kaolin, for instance, this amount of NaOH is added per unit weight of H-kaolin.

The method of determining the amounts of hydroxide to be added was thus defined. The amount of hydrochloric acid to be added to create the H-clay was not so specific. Most investigators (11) have used .05 normal hydrochloric acid, and this seems quite satisfactory. Just how much of this .05 normal acid to be used in a given case was a question which the authors had to determine. It was desired to achieve as thorough treatment as possible, of course. Because of the facility with which the hydrogen ion displaces other ions, one treatment was thought to be satisfactory, as long as hydrogen ions were present in sufficient quantity. This reasoning was in conformance with the work of Winterkorn and Moorman (10) but in the light of subsequent work, the authors believe that one treatment does not give maximum exchange, even with the hydrogen ion. The range of base exchange capacities for each of the three types of clay minerals tested has been reported by numerous investigators, with fairly close agreement. The range for kaolin, for instance, has been given as 3 to 15 milliequivalents per 100 grams by Jenny (12). In order to supply sufficient hydrochloric acid, the authors, therefore, used the following general method: enough .05 normal H Cl was

was added to supply enough H ions for the maximum reported base exchange capacity of the clay mineral in question. For example to each 100 grams of kaolin was added enough acid to supply 15 milliequivalents. This method was varied for the bentonite, as will be explained below.

Preparation of Kaolin, batch number 1

It had been found by previous tests that 100 grams of dry kaolin was enough to determine the Atterberg Constants. Therefore, 400 grams of dry kaolin was weighed for batch 1, to provide 100 grams each of H-, Na-, Ca-, and K-kaolins. As stated above, the kaolin had been ground to pass the 40 mesh sieve. The 400 grams of kaolin was added to approximately 0.6 liter of distilled water, and then thoroughly dispersed by agitating for 10 minutes with a high speed mixer. This quantity of hydrochloric acid is sufficient to supply 15 milliequivalents per 100 grams of kaolin.

When the acid was added bubbles formed on the surface of the slurry. This action continued for a few minutes and then ceased. The acid slurry was allowed to stand for 3 days, being stirred vigorously several times each day. It was noted that the clay settled rapidly in the acid slurry, leaving a clear supernatant liquid, whereas a slurry of kaolin in distilled water would not settle out completely and the supernatant liquid would remain cloudy.

At the end of the third day, the clear supernatant liquid was decanted, leaving a fairly thick slurry. To this slurry was added 6% hydrogen peroxide solution to oxidize any organic matter. Though the clay was now an H-clay, there remained excess hydrochloric acid and the chlorides formed when hydrogen displaced previously attached cations. These impurities had to be removed. Leaching with distilled water would have worked, but the sample was relatively large, and the process would have been laborious. Therefore, distilled water was added to the slurry, the mixture stirred briskly, and then allowed to settle. The clear supernatant liquid was siphoned off and tested for chlorides by the addition of silver sulphate solution. If chlorides were present, the silver would combine with the chlorine to form $Ag\ Cl_2$, a white precipitate which would cloud up the liquid. This process of washing and testing was repeated several times, soluble impurities being removed each time with the decanted liquid, until the chloride content of the removed liquid was insignificant. When the chlorine content was reduced to that of tap water, turbidities being compared by eye, the chloride content was considered as having been reduced to an insignificant amount. This test was performed, but with the kaolin and illite bond clay, a more definite end point was found.

As stated above, the kaolin settled rapidly in the acid slurry, leaving a clear supernatant liquid. After

the H-kaolin had been washed repeatedly, the clay would suddenly cease to settle out in the next wash. This change was very definite - with one washing it settled thoroughly, but upon the next addition of distilled water, the clay would no longer do so. This phenomena was due to the removal of the chlorides. When the chlorides were present in sufficient quantity, they served as flocculating agents, causing thorough sedimentation. When the electrolyte content was reduced sufficiently to make this flocculating effect negligible, complete sedimentation no longer occurred. This action was considered to be a highly satisfactory indication of sufficient washing.

The supernatant liquid of the final wash was then siphoned off, removing some of the kaolin which remained in suspension, but this was insignificant in quantity. The thick slurry which was left was H-kaolin and water.

A small amount of this H-kaolin was removed to determine exchange capacity by potentiometric titration. The titration was conducted using 0.1 normal NaOH. The hydroxide was added in uniform increments, the mixture was stirred thoroughly after each addition, and the pH was measured. A Beckman pH meter was used for these determinations, using calomel electrodes. The curve is shown in Appendix B. Exchange capacity found by this titration was 2.27 m.e. per 100 grams of kaolin. This value is just below the range of capacities reported for kaolin, but was considered satisfactory.

The remaining H-clay slurry was dried in a 105°C oven, and then ground to pass the 40 mesh sieve. One fourth of this ground material was tested to determine the Atterberg constants of the H-kaolin. The remainder was divided into three equal portions of known weight to be converted into Na-, K-, and Ca-kaolin. Each portion was dispersed in distilled water, to allow the reaction to be completed rapidly, and the desired hydroxide was added. The amount of hydroxide to be added was based on the weight of H-kaolin used and the exchange capacity of 2.27 m.e. per 100 grams as previously determined. In the case of sodium and potassium, 0.1 normal solutions were used. Calcium hydroxide is relatively insoluble and an 0.1 normal solution could not be used. Instead, a saturated solution of $Ca(OH)_2$ was used, this being .052 normal at room temperature. In all cases the pH of the sol was checked as the hydroxide was added, the final readings of pH agreeing closely with the pH corresponding to the exchange capacity of 2.27 m.e. per 100 grams in the potentiometric titration. The Ca-, K-, and Na-clay sols thus formed were dried at 105°C, ground to pass the 40 mesh sieve, and tested.

Batch number 2

A small batch, number 2, was prepared in exactly the same way as batch number 1 to see if the Atterberg Constants for the H-clay could be reproduced. Exact agreement was obtained.

Batch number 3

The Atterberg Constants were determined for all four homoionic clays made in batch number 1. The Na-kaolin, having been tested, was reground and tested again, to see if results could be reproduced. The first test which was considered good, gave a liquid limit of 37.3%. The second test, also considered good, gave a liquid limit of 32.7%. This discrepancy was surprising and at first could not be explained. A third test was made, after another grinding, giving a liquid limit of 33.0%, close agreement with test number two. However, test number one was too good to be arbitrarily dismissed, and so further investigation was called for. This investigation led to the belief that something in the process of wetting, drying thoroughly, and regrinding caused some effect on the Atterberg Constants. This effect was attributed to the grinding; kaolin is affected by grinding according to Laws and Page (13). In the light of such facts, it was decided to prepare a third batch of kaolin, this time dispensing with the drying and grinding which was used in batch number one in order to facilitate mixing and testing.

Subsequent to the preparation of batch number one, it was discovered that more complete exchange could be obtained by treating twice with hydrochloric acid. Also the filter apparatus which had been required to

prepare the bentonite samples was still available, and it was decided to leach hydrochloric acid through the kaolin to increase exchange.

A fresh lot of kaolin was taken, and the lumps were ground to pass the 40 mesh sieve. This grinding was required but was the only one used in batch number 3. The kaolin was then placed in the Buchner filter funnels and 1 liter of 0.05 normal hydrochloric acid per 100 grams of kaolin was leached through. The advantage of the filtration method is that the replaced cations are removed as they are liberated. Leaving the released cations in the presence of the clay represses further exchange. The filtration was considerably more time consuming than was expected, so that process was ceased. In order to insure thorough exchange, the kaolin was then subjected to the treatment used to prepare batch number 1.

The H-kaolin thus formed had been subjected to two treatments, and it was expected that the exchange capacity measured by titration would be increased. Such was the case, the capacity being found as 4.4 m.e. per 100 grams as compared to 2.27 m.e. per 100 grams for batch 1.

The H-kaolin slurry was divided into four equal portions. The H-kaolin was tested by drying slowly down to the plastic range, without allowing the clay to harden completely. Therefore, no grinding was

necessary. The remaining 3 portions were converted into the Na-, K-, and Ca- kaolins by the usual method. Testing was again conducted by drying down to the plastic range but never allowing complete dehydration. Thus, batch number 3 was made and tested with only the original grinding.

Illite

The illite was prepared using the same general method as used for kaolin batch 1. The hydrogen peroxide solution was added to the slurry before the acid in the case of the illite, however. Two separate batches were prepared, using 600 grams for batch 1 and 500 grams for batch 2. Each was treated with hydrochloric acid one time. The maximum reported capacity for illite is 40 m.e. per 100 grams, and sufficient acid was provided to supply this amount. The exchange capacity determined for batch 1, using 0.1 normal sodium hydroxide as usual, was 10.52 m.e. per 100 grams and for batch 2 it was 10.75 m.e. per 100 grams. Samples were tested by drying into the plastic range without allowing complete dehydration. A test was also conducted on the K-illite after drying and regrinding, with results agreeing closely.

It was found that in order to obtain a satisfactory titration curve, considerable care had to be used. The variable speed mixer was used with a glass stirrer to keep the mixture agitated during addition of the hydroxide.

The hydroxide was added in small, uniform increments, the mixture was stirred for one minute, and the pH was recorded. This one minute delay allowed the pH to settle down to a final value, and so the titration curve took characteristic shape. The first test had been conducted without standardizing the time interval between addition of the hydroxide and determination of the pH, and the curve was unsatisfactory.

As noted above, the illite showed the same phenomena as the kaolin when the washings were conducted to remove the excess hydrochloric acid and the chlorides. When the chloride content had been reduced sufficiently, the illite no longer settled out completely. No further washings were used, therefore.

Bentonite Batch number 1

It was expected that preparation of the bentonite would involve the most difficulty, and such was the case. Previous tests had shown that 25 grams of bentonite was enough for determination of the Atterberg Constants. Accordingly, 100 grams of the bentonite was prepared in the first batch. A moisture content determination of air-dry bentonite gave a 15% water content. Therefore, the 100 grams of air-dry bentonite contained 87.0 grams of oven dry bentonite. The bentonite was dispersed in 2.8 liters of distilled water by high speed mixer, the resulting sol having a consistency of light motor oil. This sol was allowed to stand for 2 days to reach hydration

equilibrium. At this time 1 liter of .05 normal hydrochloric acid was added. The pH of the resulting sol was measured and found to be 2.75. Because of this low pH, no more acid was added to prevent the breakdown of the lattice structure as explained by McBain (14). The sol was allowed to stand for a day and the pH was found to be 2.75 still. Therefore, no more acid was added. No settlement had occurred during this time, but a very definite color change was noted. Before adding the acid, the sol had a brownish yellow color. After the acid had been added and the sol allowed to stand for a day, the color had changed to a light gray. There was no doubt that some significant change had taken place.

The problem then confronting the investigators was to separate the H-bentonite from the excess acid and the chlorides. With the kaolin and illite, sedimentation solved this problem. With the bentonite, however, settling did not take place. It has been stated previously that montmorillonite swells enormously when fully hydrated. It can adsorb tremendous quantities of water. This hydration had taken place, and the sol which originally was quite fluid became more viscous. When it became obvious that the bentonite was not going to settle out, some of the sol was siphoned off and subjected to high speed centrifuging for thirty minutes. This caused a slight amount of settling, but the method obviously would not be satisfactory. The only remaining possibility

seemed to be filtration. A battery of Buchner funnels was set up for vacuum filtration. As the filter papers became impregnated with the bentonite, the flow rate was reduced greatly. As often as practicable, the gel which had collected on the filter paper was scraped off and saved. The water content of this bentonite gel was approximately 1000 per cent, but it was the best that could be done. The first filtration was completed in 24 hours. The gel which had been collected was dispersed in distilled water by the variable speed mixer and the resulting sol was filtered, the gel removed and the process repeated. This was continued until the filtrate contained an insignificant amount of chlorides using the silver sulphate test as before.

The gel collected after the final wash was H-bentonite. A small portion was removed, dispersed in distilled water, and a potentiometric titration was conducted, using 0.1 normal NaOH as before. The curve is shown in Appendix B. The exchange value thus determined was 34.5 m.e. per 100 grams.

The H-bentonite was oven dried at 105°C and ground to pass the 40 mesh sieve. It was found that a considerable portion of the bentonite had been lost in the process of filtering, there being only 40 grams of H-bentonite collected from batch 1. This was not enough to prepare all of the required homoionic specimens, and therefore a second batch was prepared using the same method used for batch one.

The H-bentonite was dried, ground to pass the 40 mesh sieve, and tested for its Atterberg Constants. The remaining H-bentonite was made into Na-, K-, and Ca-bentonites by the usual method. All homoionic clays were dried, ground to pass the 40 mesh sieve, and tested.

The H- bentonite gel, as previously noted had a light gray color. The Na-bentonite gel had a brownish yellow color, resembling the as-received bentonite. The K-bentonite was brownish-yellow also, but lighter in color than either the Na- or the as-received bentonite. The Ca- bentonite in the plastic range resembled a putty more than a gel, and had a light gray color similar to the H- bentonite. This putty-like quality of the Ca- bentonite was very noticable, as contrasted with the gelatinous characteristics of the other bentonites.

TESTING

Testing in General

All clays were tested in the standard Casagrande machine for the determination of the liquid limits. This machine is described in detail in A.S.T.M. specifications as well as the procedure. Basically, the testing consisted of placing the well mixed clay and water in the bowl of the tester, cutting it with the special knife to make a groove, and cranking until the groove closed. The clay-water mixture was thoroughly mixed and homogeneous throughout. The best method of transferring the clay to the tester was found to be with a spatula. The top of the clay was smoothed prior to cutting. The quantity of material placed in the tester was such that when cut with the special knife, a groove one centimeter deep was formed. The cut was made quickly and cleanly as slow cutting left jagged edges on the groove. Special care was taken when cutting to insure that the knife was at all times bearing on the bottom of the bowl. This action meant a clean bottom in the cut, which was found to be very important. It was discovered that, should any soil or water still remain joining the sides in the bottom of the groove, the number of blows required to close the groove was materially reduced. In a like manner, the depth of the cut was always kept at one centimeter as a deeper or shallower cut influenced the number of blows to closing. The actual testing

was commenced immediately after cutting at a blow rate of two per second. The test was considered complete when the groove was closed for a distance of one-half inch. The number of blows to close was then recorded, and the groove was smeared together again. The entire procedure was then performed again. This process was repeated three times for each moisture content for the purpose of checking. Testing was thus conducted at various water contents, water being either added or removed as necessary. A minimum of six such tests was performed for each liquid limit. At the conclusion of each test a small sample of the soil was removed from the closed groove and placed in a weighing can for a moisture content determination. A recommended form for the recording of all this test data appears in Appendix A of this paper.

With the moisture content and the number of blows known, a flow curve was drawn to determine the liquid limit. These curves for all clays tested appear in Appendix C. A glance at any one of these curves will quickly explain the manner in which they were constructed. The number of blows for each moisture content was plotted along the logarithmic abscissa while the moisture content was plotted directly above to a linear scale. A line was then drawn through these points, and the moisture content for twenty-five blows was determined. The moisture content is by definition the liquid limit.

Such a line is called a flow line (or curve). The slope of this line is the flow index.

Plastic limits were determined from the same soil as that tested for the liquid limits. The soil was dried to the proper consistency and then tested. Testing was conducted by kneading the soil in the hands, rolling it into one-eighth inch threads on a glazed porcelain plate, and then kneading again. This procedure was continued until the one-eighth inch threads would break when rolled out. The broken threads were then placed in a weighing can and the moisture content determined. Three such tests were made for each plastic limit as a check.

Knowing the liquid limit and plastic limit, the plastic index was found by subtracting the latter from the former. The toughness index was calculated by dividing the plastic index by the flow index. The flow index is used as a measure of the steepness of the flow line. Clays having steep flow lines will have high flow indices. This means that for a small change in the number of blows required to close the groove there is a large change in the moisture content. The toughness index is used to evaluate the differences in shearing strength that various clays have at the plastic limit.

Testing of Kaolinite

The kaolinite, having been received in lump form, was ground in a manual grinder and sieved through a

40 mesh sieve (ASTM). All clays were tested in the natural state so as to become familiar with the actions of the clay and to have test results with which the results from the prepared samples may be compared. No difficulty was encountered in working with kaolinite. The lumps were easily ground, the clay mixed nicely with water, and tested with ease.

Three batches of kaolinite were prepared as explained before. The first batch was tested with one grinding for the H-kaolinite and two grindings for the Na, Ca, and K-kaolinite. These grindings were in addition to the original grinding which reduced the lumps. The H-clay was dried and ground to pass the 40 mesh sieve.

A fraction was selected for testing. The remainder was divided into three equal parts from which the Na, K, and Ca-kaolinite were prepared. These clays were ground again to prepare them for testing, hence, the extra grinding. All tests were made by adding water to the ground clay until the proper consistency was attained. When the test was completed on the first batch of kaolinite, a check was made on the Na-kaolinite and the K-kaolinite after giving them still another grinding. The results obtained were not consistent. As a further check a second small batch of kaolinite was prepared. This was tested for the H-clay only, and the results checked. It was thought that re-grinding had affected the results. Since for the first

batch the H-clay had only one grinding and the others two, it was thought necessary to prepare still another batch which would be tested with only one grinding, this one being the one used to reduce the lumps. More of the effect of regrinding will be taken up in the section of this paper dealing with results.

As pointed out before, the third batch of kaolinite was treated twice with H Cl while the first and second batches were only treated once. This extra treatment was made in order to increase the exchange of the clay and thereby accentuate the effect of the cations on Atterberg's constants. This third batch was never allowed to harden after its initial dispersion. Tests were conducted by decreasing the moisture content until the range of plasticity was reached whereupon they were tested. Results for the first and third batches are given in the Appendices.

Testing of Illite

The illite bond clay was received in the ground form and consequently only sieving was required. Tests conducted on the clay as received indicated that there would be no difficulty in the testing of this clay. The illite bond clay was tested in the same manner as the kaolinite. The illite tested nicely for all ions. In the plastic range the clay was slightly sticky and would sometimes adhere to the cutting tool. In such cases the groove was immediately closed with a spatula and

another cut made. Frequently, during a test the illite would tend to set up as exhibited by the large number of blows required to close the groove when on the test before at the same moisture content, a much smaller number had sufficed. In such cases the clay was re-worked in the Casagrande machine with a spatula and several more tests conducted. Instead of only three tests at any one moisture content, as many as ten were performed and the number of blows occuring most frequently was selected.

Two batches of illite were prepared. From the first batch the H and Na-illite were tested; from the second batch the Ca and K-illite were tested. A check was made between the two batches by also testing the H-clay from the second batch and comparing it with the first batch H clay. Results checked well. All illite tests were conducted by decreasing the moisture content down into the plastic range thereby eliminating regrinding.

However, a check was made to determine if regrinding would have affected the results. The untreated clay and the K-clay were selected for regrinding and tested. Results checked almost exactly with those of the first tests. Consequently, it was concluded that one regrinding did not affect the results and no further tests were conducted.

Testing of Bentonite

The bentonite, having been received in lump form was ground and sieved to pass 40 mesh. It was

immediately apparent that difficulty would be encountered with this material. When placed in water, it swelled enormously. If the clay was not added slowly to the agitated water in the dispersion cup, it would clod up and not disperse. It was found that a very slow addition of the ground clay in a fine trickle would insure complete dispersion.

Initial tests on the natural bentonite gave rise to another difficulty. As the water content of the clay was decreased, the number of blows to close the groove would steadily increase until about twenty blows were required. At this point with no change in moisture content it was possible to get any number of blows up to ninety before the groove closed. In addition it was observed that if the clay and water set in the machine for any appreciable period of time without being worked, the number of blows to close would increase again. This action was attributed to the extreme thixotropic properties reported by many investigators. These properties of the clay gave the investigators difficulty at first. Finally it was found that mixing of the clay in the tester with a spatula after every two or three tests would eliminate all of the above difficulties. With this practice it was possible to get a fairly smooth flow line. It was also found that a good flow line could be obtained by waiting a given period of time after placing the clay in the machine before cutting the clay with the knife

and testing.

With this difficulty overcome it was next found that it was possible to secure many and varied moisture contents for the liquid limit depending on how the clay was handled prior to testing. For example, if the bentonite were completely dispersed in water, allowed to set a week, and then tested by decreasing the moisture content into the plastic range it was possible to obtain very high liquid limits (about 700%). The other extreme was to add water to the ground clay and mix thoroughly by hand. The clay was then tested immediately and liquid limits of the order of 540% were obtained. Liquid limits anywhere between these two extremes could be obtained by the addition of water to take the clay into a fluid condition, waiting for a time, decreasing the moisture content, and testing. The above determinations were made on natural bentonite.

In the interests of saving time and because the Atterberg test is supposed to be a fairly rapid test, it was decided to use the method giving the lowest value for the liquid limit. As this method is not only the quickest but also the easiest, time and effort were saved.

To summarize the above, all tests on bentonite were conducted by the addition of water to the dry ground clay, mixing by hand with a spatula in a beaker or

evaporating dish and then testing. For each moisture content at least three tests were made. If results did not check, as many as fifteen tests were made and the number of blows occuring most frequently was selected as the value for that moisture content.

The use of ground dry clay for each test naturally necessitated grinding. Since it was known that the size of dry particles does not remain the same when dispersed (i.e. breaks down into much smaller particles when in contact with water), it was concluded that regrinding should have very little if any effect on this clay.

All tests gave fairly good results except for the Ca-clay. Here it was necessary to conduct another test to check the first flow line, and results agreed.

RESULTS AND CONCLUSIONS
including
Recommended Procedure for Preparation of Homoionic Clays

RESULTS AND CONCLUSIONS

General

As the name of this paper states, this investigation was concerned with the effect of cation substitution on Atterberg's Constants for certain clay minerals. It was concluded that this study must revolve about the following issues: was there any effect at all due to ionic substitution for each of the three clays studied, and if so, what was the range and direction of this effect from a given reference clay for specific conditions of sample preparation and test?

With the above in mind, the authors submit the following results. For all three clays there was a definite effect due to cation substitution. The variation in Atterberg's Constants because of such substitution is given in tabular form in this section. It is seen from this table that the cation effects are manifest only in the range of high plasticity (i.e. around the moisture content of the liquid limit), and that these effects are hardly appreciable at moisture contents around the plastic limit. Therefore, it was concluded that ionic substitution had little or no effect on the plastic limits of these three clays, but that it did have a definite effect on the range of soil plasticity as shown by the variations in the liquid limits. In a like manner it is seen from the

table that such substitution has a decided effect on the flow index. A general statement concerning this variation cannot be made, as it appears that both the type of clay and the attached cation influence this soil constant.

In summary it must be remembered that all values obtained were for the given conditions of preparation and test. More acid treatment of the clays will naturally lead to different values of Atterberg's Constants; however, the general observations and statements made immediately above will still hold.

Particular

At the outset of this study it was believed that the preparation of the samples would be fairly simple; however, such was far from the case. As the investigation progressed, it was found that a simple and concise method for the preparation of ionic clays would be of considerable value to not only the authors but also future students in soils at R.P.I. Consequently, the development of such a method is also considered to be a major result of this investigation. The following recommended procedure is, therefore, given. This procedure may be used to prepare samples for any soils apparatus.

RECOMMENDED PROCEDURE FOR PREPARATION OF HOMOIONIC CLAYS

1. Grind clay to pass 40 mesh sieve.
2. Determine weight of sample needed and increase by fifty per cent to allow for losses.
3. Disperse clay in distilled or demineralized water using electric mixer of some sort. Bentonite must be added slowly to insure complete dispersion. Enough water should be used to produce a fluid dispersion. Transfer dispersion into a large vessel, preferably glass, but necessarily a vessel resistant to acid.
4. If presence of organic matter is undesirable, add a 6% solution of hydrogen peroxide in sufficient quantity to oxidize such material. Heating and agitation will facilitate this oxidation.
5. Add .05 normal hydrochloric acid in sufficient quantity to provide at least 15 milliequivalents per 100 grams of kaolin or 40 m.e. per 100 grams of illite. For the bentonite calculate the volume of acid required on the basis of 100 m.e. per 100 grams. Do not reduce the pH of the dispersion below 3.0. (Some investigators have reported that the lattice structure of bentonites may be changed by reducing pH too low by addition of acid.) If all the acid is not used, a second treatment should be used to use this acid.

6. After the acid has been added, the clay should be stirred repeatedly over a period of several days to insure thorough exchange.
7. Kaolinite and illite will settle out when acidified and washing may be accomplished by decanting the supernatant liquid, adding distilled or demineralized water, stirring, allowing to settle, and repeating process until the chloride content of the removed liquid is approximately equal to that of tap water. Silver sulphate or silver nitrate added to a liquid containing chlorides will precipitate the chlorine in the form of the white, insoluble salt $AgCl_2$. Turbidity of the removed liquid with the added silver salt is compared with the turbidity of the tap water to which the silver compound has been added. Bentonite will not settle out and the liquid must be removed by filtration. The authors found #50 Whatman filter paper to be satisfactory. A pressure differential is required to filter, either pressure or vacuum being satisfactory. The filtrate of the bentonite is tested for chlorides in same manner as are illites and kaolinites. Several washes will be required.
8. Redisperse the chloride-free clay in distilled or demineralized water and repeat steps 5 through 7.

9. Separate a small quantity of the H-clay and disperse in distilled (demineralized) water. Conduct a potentiometric titration on the clay to determine the exchange value. Use .1 normal NaOH for this titration. Titration should be carried out with care, the hydroxide being added in uniform increments and the time interval between addition of the hydroxide and measuring of the pH being standardized. Proper increments and time intervals may best be determined by trial. Continue titration up to a pH of 10 or 11 to insure that the curve is complete and the reaction has occurred.
10. Plot test data, pH versus milliliters of added hydroxide. The point on the curve where the slope is a maximum is the point at which the reaction is considered to be complete. This point may best be located by plotting a second curve showing Δ pH per milliliter versus milliliters added. The peak point on this latter curve corresponds to the exchange value.
11. After the titration is complete, dry the sample to a constant weight at 105°C. The weight of sample used may thus be determined. Knowing the weight of sample and the milliliters of hydroxide corresponding to the exchange value, the exchange value may be computed in milliequivalents per 100 grams.

12. This exchange value may be used to compute the required amount of any other hydroxide to be added. When the computed amount of hydroxide has been added, the pH of the sol may be checked and it should be quite close to the pH corresponding to the exchange value.

(More than 2 treatments with hydrochloric acid may increase the exchange value. It is believed that the increase will be relatively small, however.)

Several other factors noted in this study are worthy of mention here. As stated earlier and as noted in the tabulated results, there is a difference in the values for batches one and three of kaolinite. This difference is due in part to regrinding and in part to the extra acid treatment given batch three. It is, therefore, recommended that the same number of grindings be used for each clay, (i.e. grind K, Na, H, etc., clays an equal number of times so as to eliminate any possible effect of regrinding on test results).

Another important observation was that the illite bond clay obviously contained only a small portion of illite. A dispersion of this clay in water with subsequent drying disclosed a very thin layer of illite on top of the dry cake with a considerable quantity of silt and other seemingly inactive fractions below. The illite bond clay in addition contained an appreciable volume of unattached cations in the form of salts which appeared on top of the dry cake in the characteristic dendritic form of crystallized soluble salts. These salts are not a permanent part of the clay as they may be removed by groundwater and yet they affect the physical properties of the soil. As a result, any test values of this clay in its untreated form must be tempered by this fact.

In supplements to this paper it will be noted that other investigations have been conducted on the prepared clays used in this study. Remarks concerning the findings of these investigators are contained therein.

ATTERBERG PLASTICITY CONSTANTS

KAOLIN

Cation	As Rec'd	H+		Na+		K+		Ca++	
Batch Number		1	3	1	3	1	3	1	3
No. of Grinding	1	2	1	3	1	3	1	3	1
Liquid Limit	43.8	42.0	41.5	37.8	31.0	36.7	31.0	37.1	35.0
Plastic Limit	26.3	22.7	22.0	23.3	21.1	24.0	22.0	21.4	20.7
Plasticity Index	17.5	19.3	19.5	14.5	9.9	12.7	9.0	15.7	14.3
Flow Index	13.0	7.5	8.5	8.0	3.2	5.6	3.5	6.7	4.5
Toughness Index	1.3	2.6	2.3	1.8	3.1	2.3	2.6	2.3	3.2

	ILLITE					BENTONITE				
Cation	AsRec'd	H+	Na+	K+	Ca++	AsRec'd.	H+	Na+	K+	Ca++
Liquid Limit	58.1	61.7	65.3	67.7	64.5	537	455	618	507	408
Plastic Limit	29.3	29.8	29.3	32.3	29.8	63.8	65.6	55.5	56.8	54.5
Plasticity Index	28.8	31.9	36.0	35.4	34.7	473.2	389.4	562.5	450.2	353.5
Flow Index	11.5	17.0	13.4	16.0	18	110	110	205	124	250
Toughness Index	2.5	1.9	2.7	2.2	1.9	4.30	3.54	2.74	3.64	1.41

NOTE: Values for liquid limits, plastic limits, and plasticity indices are expressed as per cent moisture content. Values for flow and toughness indices are dimensionless numbers.

APPENDIX A

ATTERBERG CONSTANTS DETERMINATION DATA

Atterberg Limits

Date 25 Jan. 1951

Sample No. As Received Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	23.6632	22.0868	21.1125	24.4864	25.6185	21.2208	23.7271
Wt. of Container + Dry Soil	21.5128	20.4678	19.4683	22.3628	23.2255	19.6198	21.4295
Wt. of Water	2.1504	1.6190	1.6442	2.1236	2.3930	1.6010	2.2976
Wt. of Container	16.9970	16.8851	15.6274	17.2568	16.9510	15.6025	15.5658
Wt. of Dry Soil	4.5158	3.5827	3.8409	5.1060	6.2745	4.0173	5.8637
Moisture Content %	47.6	45.2	42.8	41.6	38.1	39.9	39.2
No. of Blows	14,13,13	21,20,21	29,28,30	36,37,37	70,69,70	49,49,50	60,58,58
Container No.	42	48	36	47	22	32	27

Remarks: Dry Branch Georgia, Kaolinite

Liquid Limit 43.8%

Plastic Limit 26.3

Plastic Index 17.5

Flow Index 13.0

Toughness Index 1.35

ATTERBERG LIMITS

Date 1 March 1951

Sample No. H+ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	17.9280	20.4806	18.4004	18.9656	19.3182	20.5013	23.2419
Wt. of Container + Dry Soil	16.4513	18.3316	16.6511	17.1628	17.3455	18.3066	20.0855
Wt. of Water	1.4777	2.1490	1.7493	1.8028	1.9727	2.1947	3.1564
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	3.8090	5.3633	4.1996	4.2906	4.6351	5.1580	7.1761
Moisture Content %	38.7	40.2	41.7	42.1	42.7	42.7	44.0
No. of Blows	66,66,68	40,40,41	28,27,28	24,25,24	20,21,21	20,21,21	15,14,14
Container No.	61	88	63	76	90	73	93

Remarks: Drybranch, Georgia Kaolinite
Batch #1

Liquid Limit 42.0%

Plastic Limit 22.7%

Plastic Index 19.3%

Flow Index 7.5

Toughness Index 2.58

ATTERBLRG LIMITS

Date 6 March 1951

Sample No. Na+ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	17.7375	19.3854	19.5295	18.8700	19.2793	27.3391	21.9791
Wt. of Container + Dry Soil	16.4076	17.6220	17.6426	17.2109	17.5230	23.3777	19.5933
Wt. of Water	1.3299	1.7634	1.8869	1.6591	1.7563	3.9614	2.3858
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	3.7656	4.6537	5.1911	4.3387	4.8126	10.2291	6.6839
Moisture Content %	35.3	38.0	36.3	38.3	36.7	38.7	34.2
No. of Blows	48,48,49	22,23,23	36,35,36	20,21,21	33,34,34	19,20,20	66,66,65
Container No.	61	88	63	76	90	73	93

Remarks: Dry Branch, Georgia Kaolinite
Batch #1

Liquid Limit 37.8%

Plastic Limit 23.3%

Plastic Index 14.5

Flow Index 8

Toughness Index 1.82

ATTERBERG LIMITS

Date 8 March 1951

Sample No. K+ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	17.4556	18.8110	18.4264	19.2968	18.7440	20.6964	20.2986
Wt. of Container + Dry Soil	16.2225	17.2933	16.8482	17.5947	17.1439	18.6775	18.2727
Wt. of Water	1.2331	1.5177	1.5782	1.7021	1.6001	2.0189	2.0259
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	3.5802	4.3250	4.3967	4.7225	4.4335	5.5289	5.3633
Moisture Content %	34.5	35.0	35.1	36.1	36.1	36.7	37.7
No. of Blows	59,60,60	45,46,45	45,44,45	31,31,30	31,30,30	27,27,26	17,17,17
Container No.	61	88	63	76	90	73	93

Remarks: Dry Branch, Georgia-Kaolinite
Batch #1

Liquid Limit 36.7%

Plastic Limit 24.0

Plastic Index 12.7

Flow Index 5.6

Toughness Index 2.27

ATTERBERG LIMITS

Date 13 March 1951

Sample No. Ca++ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	23.6377	24.0254	25.6945	23.6407	22.4202	26.2115
Wt. of Container + Dry Soil	21.9787	22.2276	23.3937	21.4655	20.5370	23.5782
Wt. of Water	1.6590	1.7978	2.3008	2.1752	1.8832	2.6333
Wt. of Container	17.2541	17.1293	16.9507	15.5308	15.5582	16.9075
Wt. of Dry Soil	4.7246	5.0983	6.4430	5.9347	4.9788	6.6707
Moisture Content %	35.2	35.3	35.8	36.7	37.8	39.5
No. of Blows	50,50,51	48,49,48	42,41,42	29,30,30	21,21,22	11,11,12
Container No.	47	16	22	34	27	10

Remarks: Dry Branch, Georgia-Kaolinite
Batch #1

Liquid Limit 37.1%

Plastic Limit 21.4%

Plastic Index 15.7

Flow Index 6.7

Toughness Index 2.345

ATTERBERG LIMITS

Date 24 April 1951

Sample No. H+ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	20.6032	20.3305	20.9030	19.9857	19.5340	21.7458
Wt. of Container + Dry Soil	19.5340	19.4488	19.7650	19.2281	18.3507	19.8074
Wt. of Water	1.0692	0.8817	1.1380	0.7576	1.1833	1.9384
Wt. of Container	16.9065	17.1273	16.9482	17.2521	15.5320	15.5582
Wt. of Dry Soil	2.6275	2.3215	2.8168	1.9760	2.8187	4.2492
Moisture Content %	40.6	38.0	40.4	38.3	42.2	45.6
No. of Blows	31,31,32	65,66,67	33,33,33	58,60,57	20,20,20	10,10,10
Container No.	10	16	22	47	34	27

Remarks: Dry Branch, Georgia-Kaolinite
Batch #3

Liquid Limit 41.5

Plastic Limit 22.0

Plastic Index 19.5

Flow Index 8.5

Toughness Index 2.3

ATTERBERG LIMITS

Date 26 April 1951

Sample No. Na+ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	20.3921	20.4572	20.2640	18.7393	19.0035	21.9932
Wt. of Container + Dry Soil	19.5780	19.6888	19.4753	17.9940	18.1743	20.8445
Wt. of Water	.8141	.7684	.7887	.7453	.8292	1.1487
Wt. of Container	16.9065	17.1273	16.9482	15.5582	15.5320	17.2521
Wt. of Dry Soil	2.6715	2.5615	2.5271	2.4358	2.6423	3.5924
Moisture Content %	30.5	30.0	31.2	30.6	31.4	31.8
No. of Blows	34,34,33	50,48,49	21,20,20	29,30,32	18,18,17	15,14,15
Container No.	10	16	22	27	34	47

Remarks: Dry Branch, Georgia-Kaolinite
Batch #3

Liquid Limit 31.0

Plastic Limit 21.1

Plastic Index 9.9

Flow Index 3.2

Toughness Index 3.09

ATTERBERG LIMITS

Date 26 April 1951

Sample No. K+ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	15.4310	16.2591	16.1970	15.9880	16.4166	19.4035
Wt. of Container + Dry Soil	14.7178	15.5183	15.4240	15.2733	15.5318	17.8085
Wt. of Water	.7132	.7408	.7730	.7147	.8848	1.5950
Wt. of Container	12.4450	13.0658	12.8683	12.9450	12.7080	12.9070
Wt. of Dry Soil	2.2728	2.4525	2.5557	2.3283	2.8238	4.9015
Moisture Content %	31.4	30.2	30.3	30.7	31.4	32.6
No. of Blows	21,20,20	39,40,39	37,37,39	31,31,32	19,19,20	10,10,10,10
Container No.	63	66	76	89	90	93

Remarks: Dry Branch, Georgia, Kaolinite
Batch #3

Liquid Limit 31.0

Plastic Limit 22.0

Plastic Index 9.0

Flow Index 3.5

Toughness Index 2.6

ATTERBERG LIMITS

Date 3 May 1951

Sample No. Ca++ Kaolinite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	20.2340	20.4227	20.3900	19.0500	18.6700	20.6401
Wt. of Container + Dry Soil	19.4065	19.6051	19.5140	18.1616	17.8523	19.7277
Wt. of Water	.8275	.8176	.8760	.8884	.8177	.9124
Wt. of Container	16.9065	17.1273	16.9482	15.5582	15.5320	17.2521
Wt. of Dry Soil	2.5000	2.4778	2.5658	2.6034	2.3203	2.4756
Moisture Content %	33.1	33.0	34.2	34.1	35.2	36.8
No. of Blows	66,66,64	69,70,70	35,36,36	36,37,37	22,23,24	10,11,10
Container No.	10	16	22	27	34	47

Remarks: Dry Branch, Georgia-Kaolinite
Batch #3

Liquid Limit 35.0

Plastic Limit 20.7

Plastic Index 17.3

Flow Index 4.5

Toughness Index 3.2

ATTERBERG LIMITS

Date 27 February 1951

Sample No. As received Illite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	24.5492	22.0023	21.8406	23.8391	23.5781	22.8550	22.6303
Wt. of Container + Dry Soil	20.4570	18.7611	18.4269	19.8409	19.5710	19.2807	18.8974
Wt. of Water	4.0922	3.2412	3.4137	3.9982	4.0071	3.5753	3.7329
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	7.8147	5.7928	5.9754	6.9687	6.8606	6.1321	5.9880
Moisture Content %	52.4	55.8	57.0	57.2	58.3	58.4	62.4
No. of Blows	80,85,84	42,42,41	31,32,32	32,32,32	24,23,24	24,24,25	11,11,11
Container No.	61	88	63	76	90	73	93

Remarks: Joliet, Illinois-Illite

Liquid Limit 58.1%

Plastic Limit 29.3

Plastix Index 28.8

Flow Index 11.5

Toughness Index 2.51

ATTERBERG LIMITS

Date 10 March 1951

Sample No. H+ Illite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	19.8154	22.0842	18.9355	24.5777	21.8252	24.7497	25.1627
Wt. of Container + Dry Soil	17.2512	18.7195	16.4283	20.1609	18.4374	20.2557	20.3064
Wt. of Water	2.5642	3.3647	2.5072	4.4168	3.3878	4.4940	4.8563
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	4.6089	5.7512	3.9768	7.2887	5.7270	7.1071	7.3970
Moisture Content %	55.6	58.5	62.8	60.6	59.2	63.3	65.6
No. of Blows	56,54,56	38,39,40	22,21,23	29,29,30	36,35,35	20,19,20	14,15,15
Container No.	61	88	63	76	90	73	93

Remarks: Joliet, Illinois-Illite

Liquid Limit 61.7%

Plastic Limit 29.8%

Plastic Index 31.9

Flow Index 17.0

Toughness Index 1.875

ATTERBERG LIMITS

Date 17 March 1951

Sample No. Na+ Illite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	20.7449	22.6021	20.7594	19.7182	18.3265	21.1026	22.8967
Wt. of Container + Dry Soil	17.7117	18.9188	17.5516	17.0226	16.1807	18.0516	18.8662
Wt. of Water	3.0332	3.6833	3.2078	2.6956	2.1458	3.0510	4.0305
Wt. of Container	12.6423	12.9683	12.4575	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	5.0694	5.9505	5.1001	4.1504	3.4703	4.9030	5.9568
Moisture Content %	59.7	61.8	62.9	65.	61.8	62.3	67.7
No. of Blows	64,66,67	47,46,46	37,38,38	26,27,26	47,47,47	41,40,41	17,17,1
Container No.	61	88	63	76	90	73	93

Remarks: Joliet, Illinois-Illite

Liquid Limit 65.3 %

Plastic Limit 29.3

Plastic Index 36.0

Flow Index 13.4

Toughness Index 2.69

ATTERBERT LIMITS

Date 13 March 1951

Sample No. K+ Illite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	19.8202	20.0764	21.2495	20.7942	20.7890	22.7322	22.8970
Wt. of Container + Dry Soil	17.0471	17.3143	17.8210	17.6786	17.5815	18.8736	18.7276
Wt. of Water	2.7731	2.7621	3.4285	3.1156	3.2075	3.8586	4.1694
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	4.4048	4.3460	5.3695	4.8064	4.8711	5.7250	5.8182
Moisture Content %	62.8	63.6	63.8	63.5	65.7	67.4	71.6
No. of Blows	49,50,50	42,42,43	40,41,41	45,45,44	31,32,32	25,25,26	14,13,14
Container No.	61	88	63	76	90	73	93

Remarks: Joliet, Illinois-Illite

Liquid Limit 67.7%

Plastic Limit 32.3

Plastic Index 35.4

Flow Index 16.0

Toughness Index 2.21

ATTERBERG LIMITS

Date 3 March 1951

Sample No. Ca++ Illite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	24.7405	24.1145	27.0917	23.8103	21.6297	26.4138	22.1744
Wt. of Container + Dry Soil	21.7190	21.4300	23.1650	20.5400	19.1900	22.6255	18.5444
Wt. of Water	3.0215	2.6845	3.9267	3.2703	2.4397	3.7883	3.6300
Wt. of Container	16.9065	17.1273	16.9482	15.5582	15.5320	17.2521	13.0702
Wt. of Dry Soil	4.8125	4.3027	6.1168	4.9818	3.6580	5.3734	5.4742
Moisture Content %	62.8	62.4	64.2	65.6	66.7	70.6	66.4
No. of Blows	30,29,30	33,33,33	26,26,26	22,22,21	18,19,19	11,11,12	19,19,19
Container No.	10	16	22	27	34	47	66

Remarks: Joliet, Illinois-Illite

Liquid Limit 64.5%

Plastic Limit 29.8

Plastic Index 34.7

Flow Index 18

Toughness Index 1.93

ATTERBERG LIMITS

Date 24 March 1951

Sample No. As Received Bentonite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	18.7413	20.2432	18.9598	19.7115	19.2785	21.2826
Wt. of Container + Dry Soil	13.5555	14.0801	13.4896	13.9686	13.7993	14.5596
Wt. of Water	5.1858	6.1631	5.4702	5.7429	5.4792	6.7230
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486
Wt. of Dry Soil	.9132	1.1118	1.0381	1.0964	1.0889	1.4110
Moisture Content %	568	555	527	525	503	476
No. of Blows	12,13,12	17,17,18	30,30,29	30,30,31	45,48,47	78,80,74
Container No.	61	88	63	76	90	73

Remarks: Rock River, Wyoming-bentonite

Liquid Limit 537%

Plastic Limit 63.8

Plastic Index 473.2

Flow Index 110

Toughness Index 4.30

ATTERBERG LIMITS

Date 3 April 1951

Sample No. H+ Bentonite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	17.2940	17.5695	16.7460	18.3434	17.3564	18.6324
Wt. of Container + Dry Soil	13.3861	13.7529	13.2062	13.9111	13.5803	14.1486
Wt. of Water	3.9079	3.8166	3.5398	4.4323	3.7761	4.4838
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486
Wt. of Dry Soil	.7438	.7846	.7547	1.0389	.8699	1.0000
Moisture Content %	526	487	470	416	434	448
No. of Blows	7,7,7	14,15,14	17,17,18	51,55,56	35,37,36	28,29,29
Container No.	61	88	63	76	90	73

Remarks: Rock River, Wyoming bentonite

Liquid Limit 455%

Plastic Limit 65.6

Plastic Index 389.4

Flow Index 110

Toughness Index 3.54

ATTERBERG LIMITS

Date 7 April 1951

Sample No. Na+ Bentonite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	22.4950	23.1082	23.7792	22.3600	21.9666	24.9780
Wt. of Container + Dry Soil	17.7772	18.0355	17.8950	16.3913	16.3878	18.4764
Wt. of Water	4.7178	5.0727	5.8842	5.9687	5.5788	6.5016
Wt. of Container	16.9065	17.1273	16.9482	15.5582	15.5320	17.2521
Wt. of Dry Soil	.8707	.9082	.9468	.8431	.8558	1.2243
Moisture Content %	542	559	622	708	652	531
No. of Blows	52,55,54	50,49,50	22,22,22	9,9,9	18,18,18	60,64,64
Container No.	10	16	22	27	34	47

Remarks: Rock River, Wyoming Bentonite.

Liquid Limit 618%

Flow Index 205%

Plastic Limit 55.5

Toughness Index 2.74

Plastic Index 562.5

ATTERBERG LIMITS

Date 10 April 1951

Sample No. K+ Bentonite

Purpose of test: Liquid Limit

Wt. of Container + Wet Soil	18.8005	18.1663	17.3584	18.9740	17.9057	20.0149	19.5544
Wt. of Container + Dry Soil	13.5976	13.7844	13.2391	13.8756	13.5819	14.4181	14.0829
Wt. of Water	5.2029	4.3819	4.1193	5.0984	4.3238	5.5968	5.4715
Wt. of Container	12.6423	12.9683	12.4515	12.8722	12.7104	13.1486	12.9094
Wt. of Dry Soil	.9553	.8161	.7876	1.0034	.8715	1.2695	1.1735
Moisture Content %	543	537	522	507	495	441	467
No. of Blows	12,12,12	17,17,17	20,21,20	23,22,23	29,30,31	79,80,80	50,50,49
Container No.	61	88	63	76	90	73	93

Remarks: Rock River, Wyoming - Bentonite

Liquid Limit 507%

Plastic Limit 56.8

Plastic Index 450.2

Flow Index 124

Toughness Index 3.64

ATTERBERG LIMITS

Date 12 April 1951

Sample No. Ca++ Bentonite

Purpose of Test: Liquid Limit

Wt. of Container + Wet Soil	16.3655	16.9446	18.6318	18.1418	17.3183	17.7980	17.4250
Wt. of Container + Dry Soil	13.3075	13.6847	13.5852	13.9220	13.6153	14.2828	13.9122
Wt. of Water	3.0580	3.2599	5.0466	4.2198	3.7030	3.5152	3.5128
Wt. of Container	12.6423	12.9683	12.4515	12.8683	12.7104	13.1486	12.9094
Wt. of Dry Soil	.6652	.7164	1.1337	1.0537	.9049	1.1342	1,0028
Moisture Content %	458	455	443	402	408	310	349
No. of Blows	16,15,16	16,16,15	18,18,17	25,26,26	25,25,26	61,59,60	42,40,41
Container No.	61	88	63	76	90	73	93

Remarks: Rock River, Wyoming-Bentonite

Liquid Limit 408%

Plastic Limit 54.5

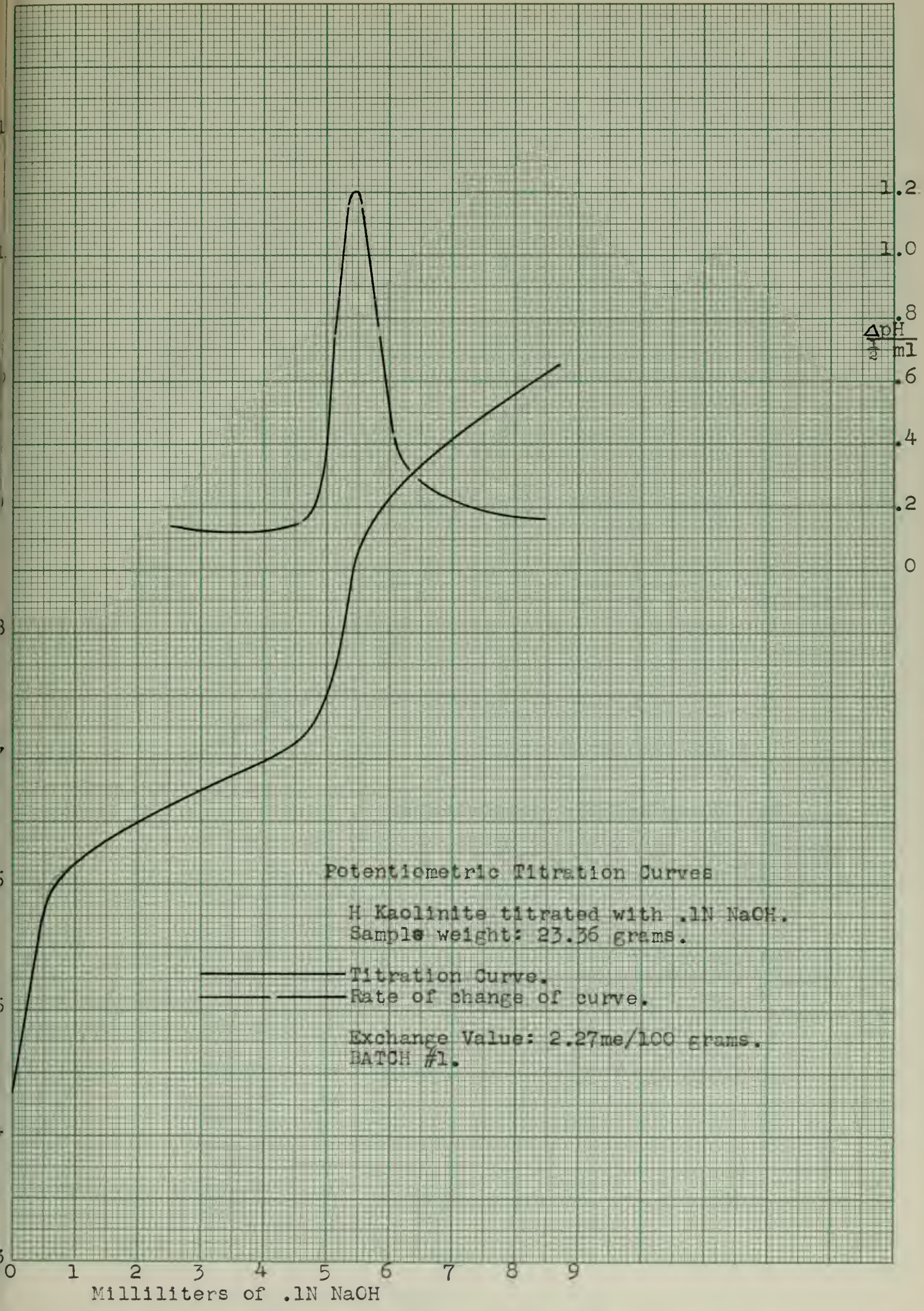
Plastic Index 353.5

Flow Index 250

Toughness Index 1.41

APPENDIX B

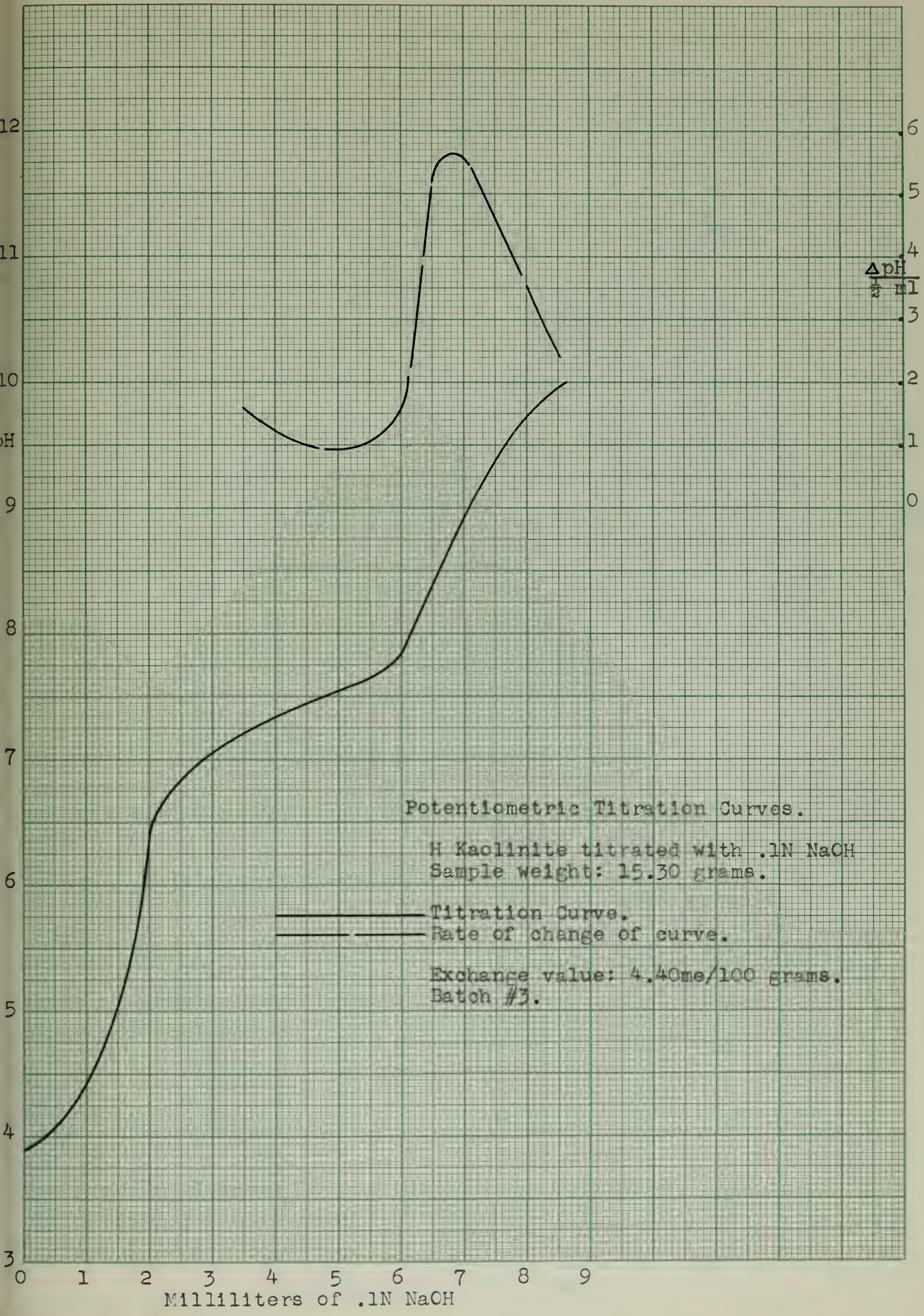
POTENTIOMETRIC TITRATION CURVES



Potentiometric Titration Curves

H Kaolinite titrated with .1N NaOH.
Sample weight: 23.36 grams.

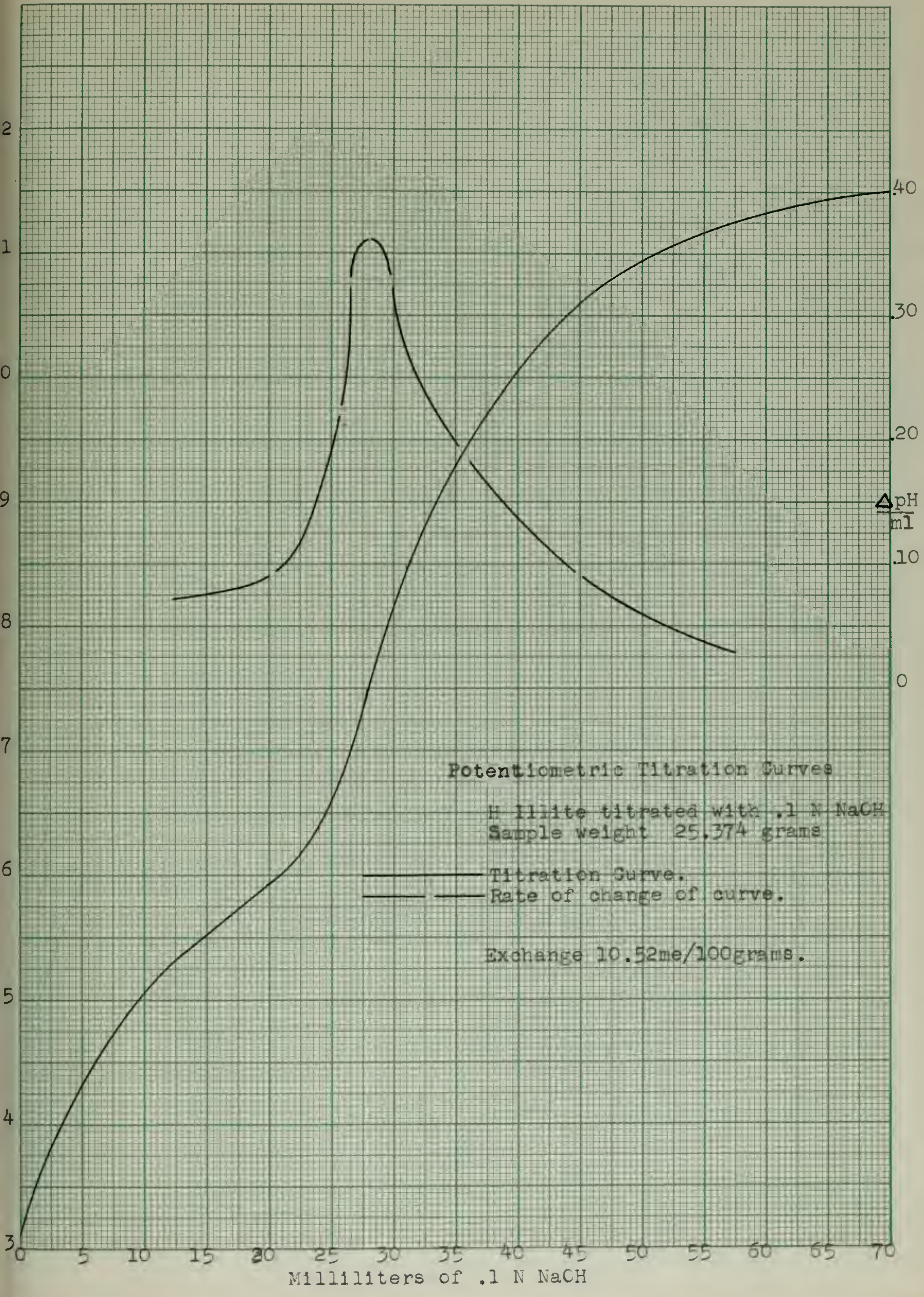
Exchange Value: 2.27me/100 grams.
BATCH #1.



Potentiometric Titration Curves.

H Kaolinite titrated with .1N NaCH
Sample weight: 15.30 grams.

Exchange value: 4.40me/100 grams.
Batch #3.

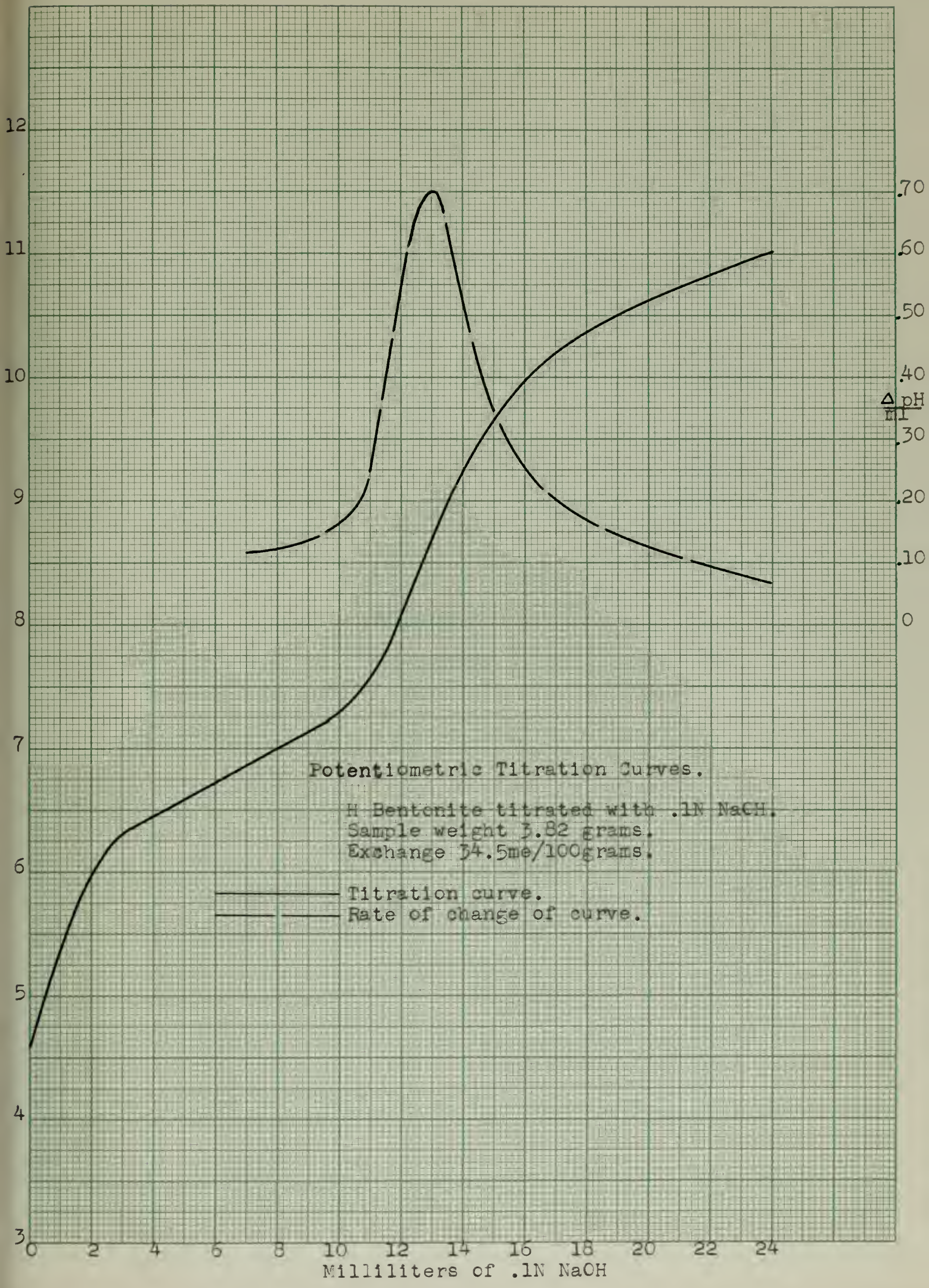


Potentiometric Titration Curves

H Illite titrated with .1 N NaCH
Sample weight 25.374 grams

Titration Curve.
Rate of change of curve.

Exchange 10.52me/100grams.

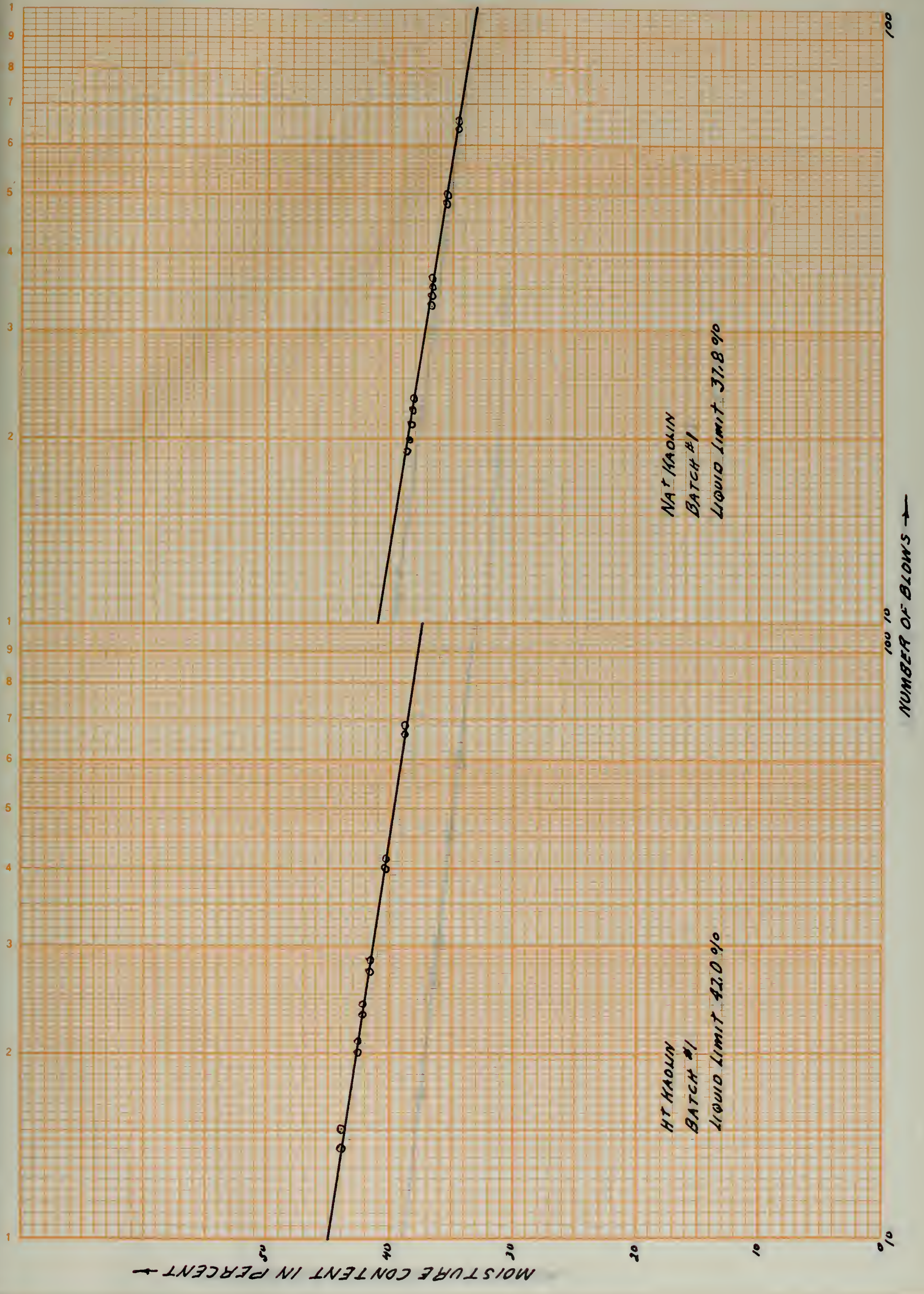


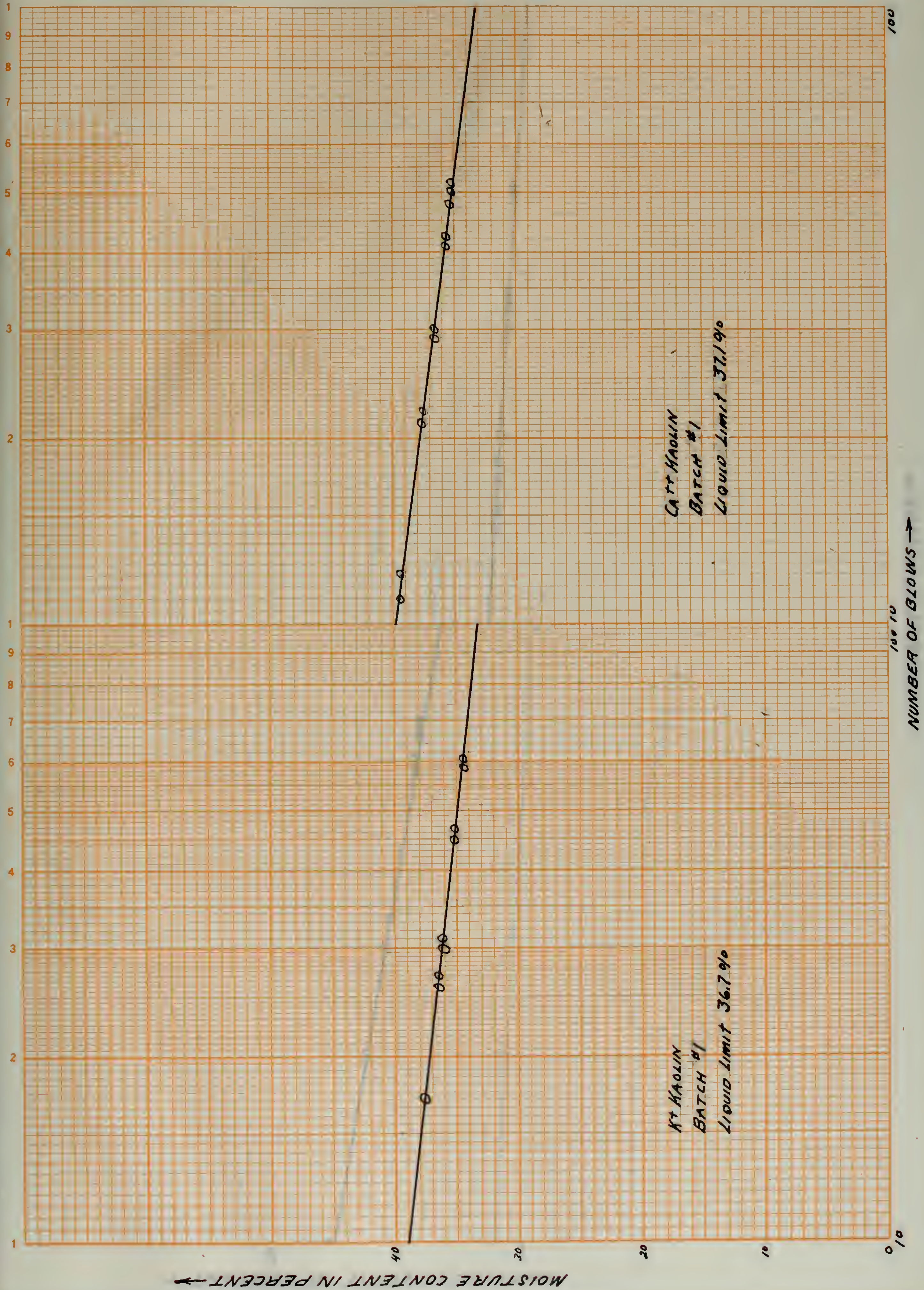
Potentiometric Titration Curves.

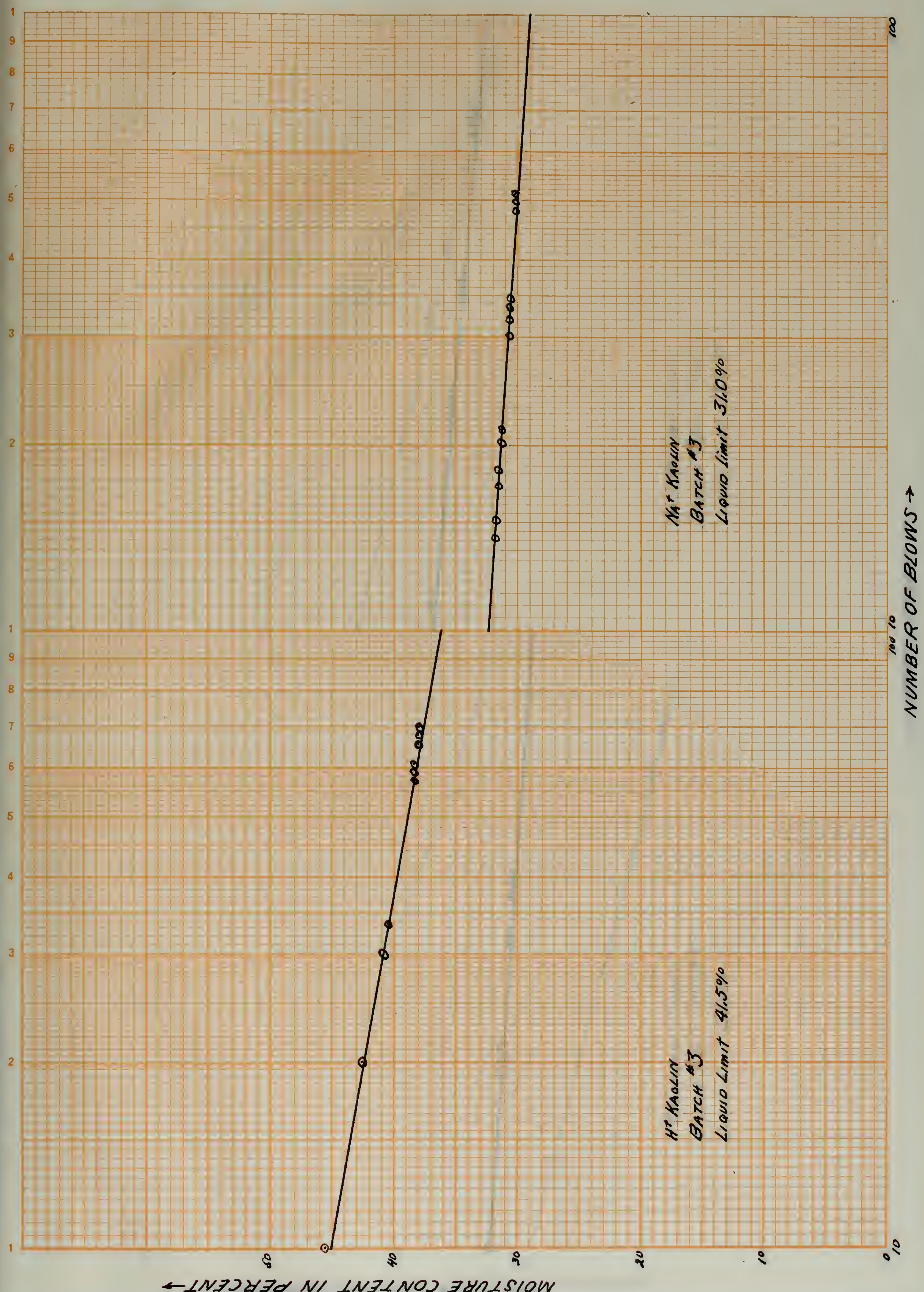
H Bentonite titrated with .1N NaOH.
Sample weight 3.82 grams.
Exchange 34.5me/100grams.

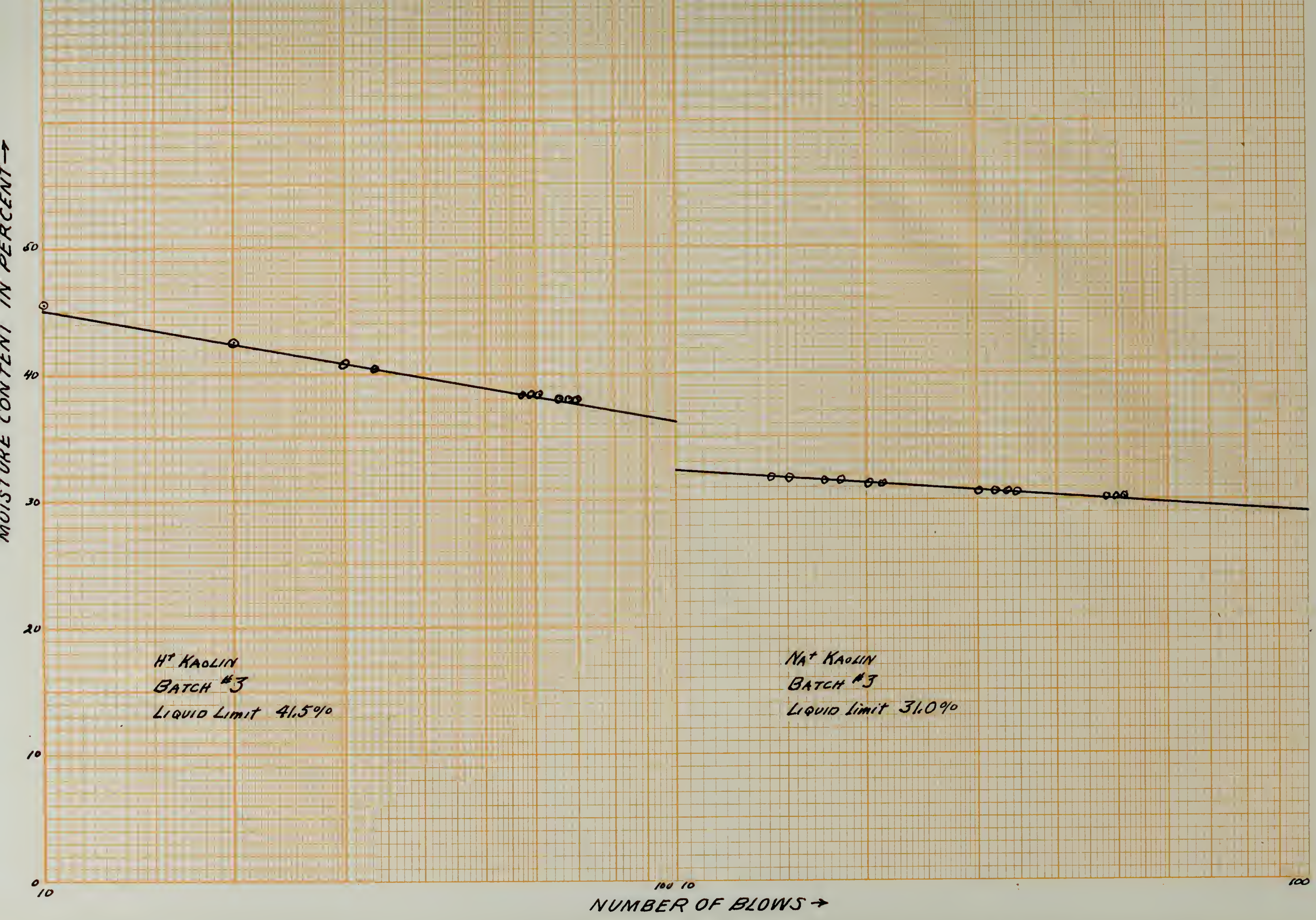
APPENDIX C

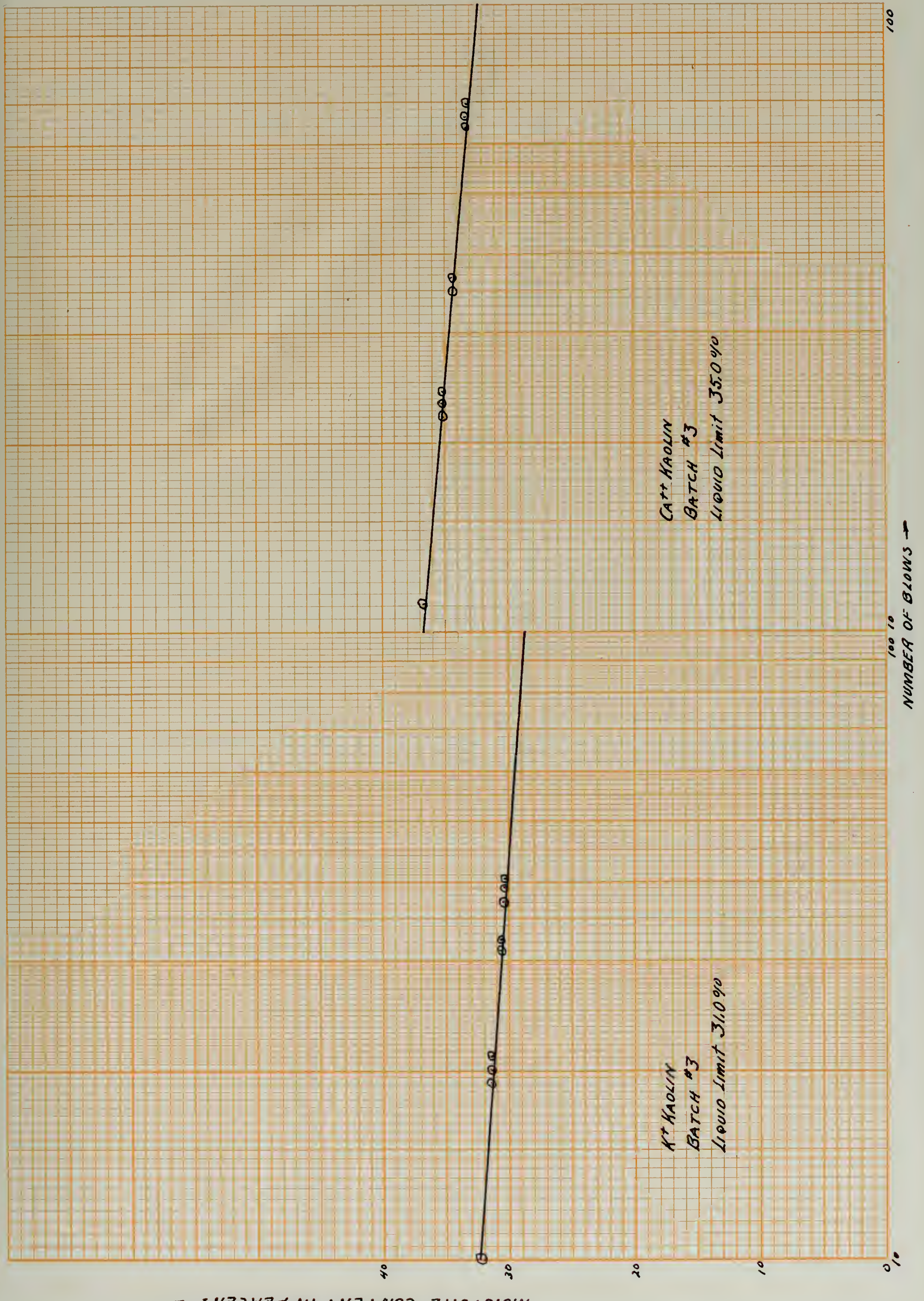
FLOW CURVES

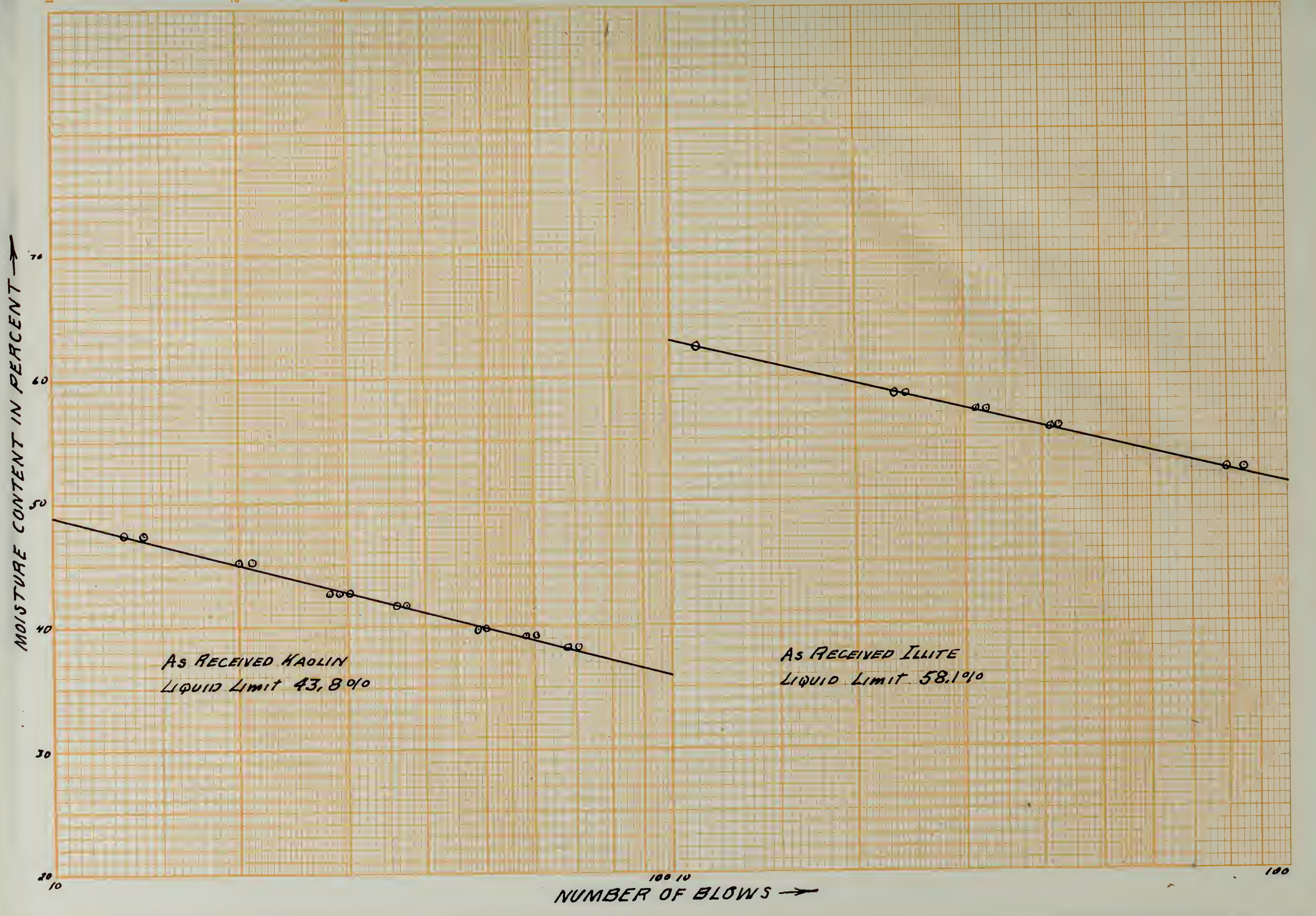
NA+ KAOLIN
BATCH #1
LIQUID LIMIT 37.8 %
H+ KAOLIN
BATCH #1
LIQUID LIMIT 42.0 %
NUMBER OF BLOWS →
MOISTURE CONTENT IN PERCENT →
100
10
100
10
50
40
30
20
10
0
1
9
8
7
6
5
4
3
2
1

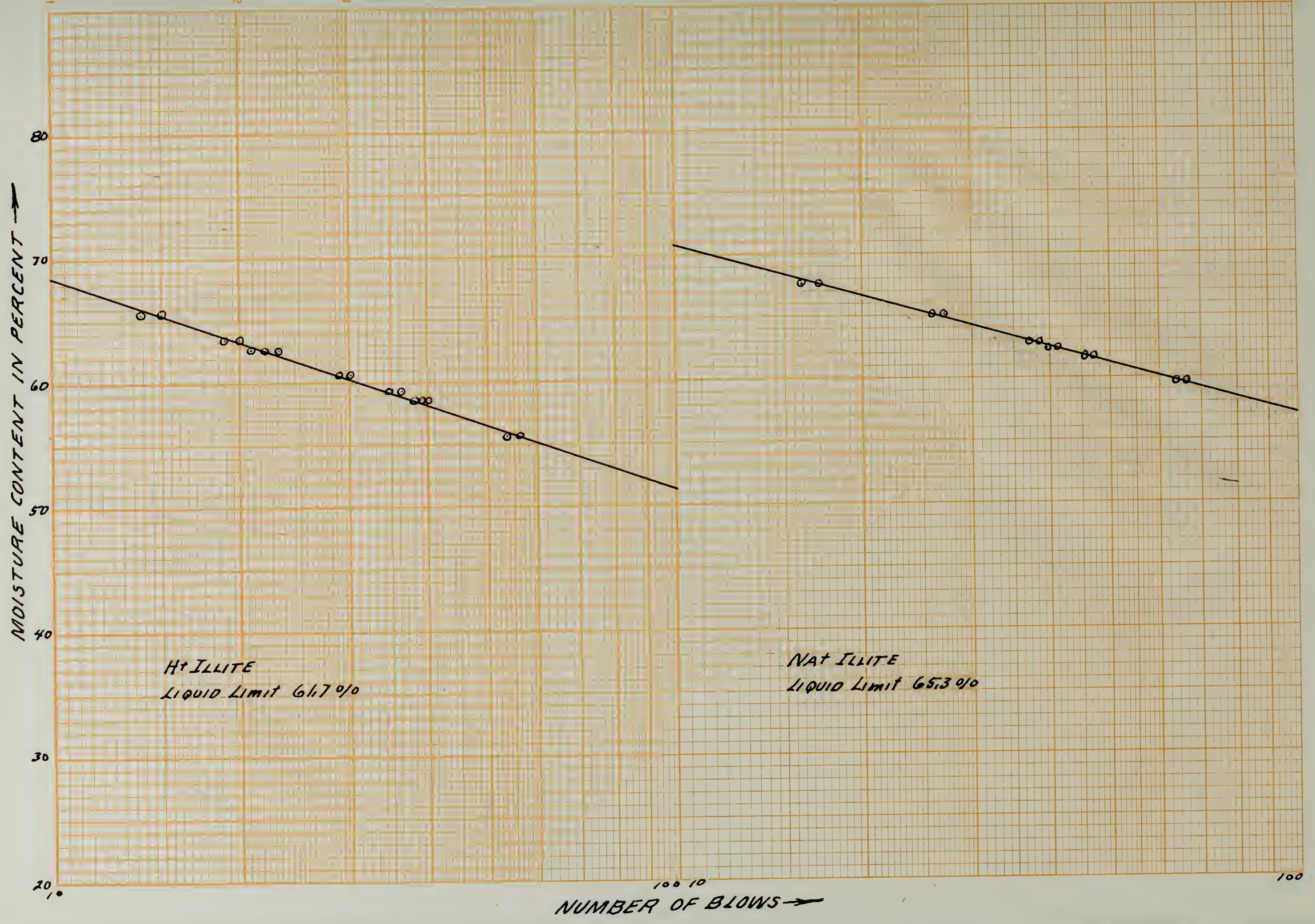

Ca++ Kaolin
Batch #1
Liquid Limit 37.1%
K+ Kaolin
Batch #1
Liquid Limit 36.7%
NUMBER OF BLOWS →
MOISTURE CONTENT IN PERCENT →
40
30
20
10
0
10
100
1
2
3
4
5
6
7
8
9

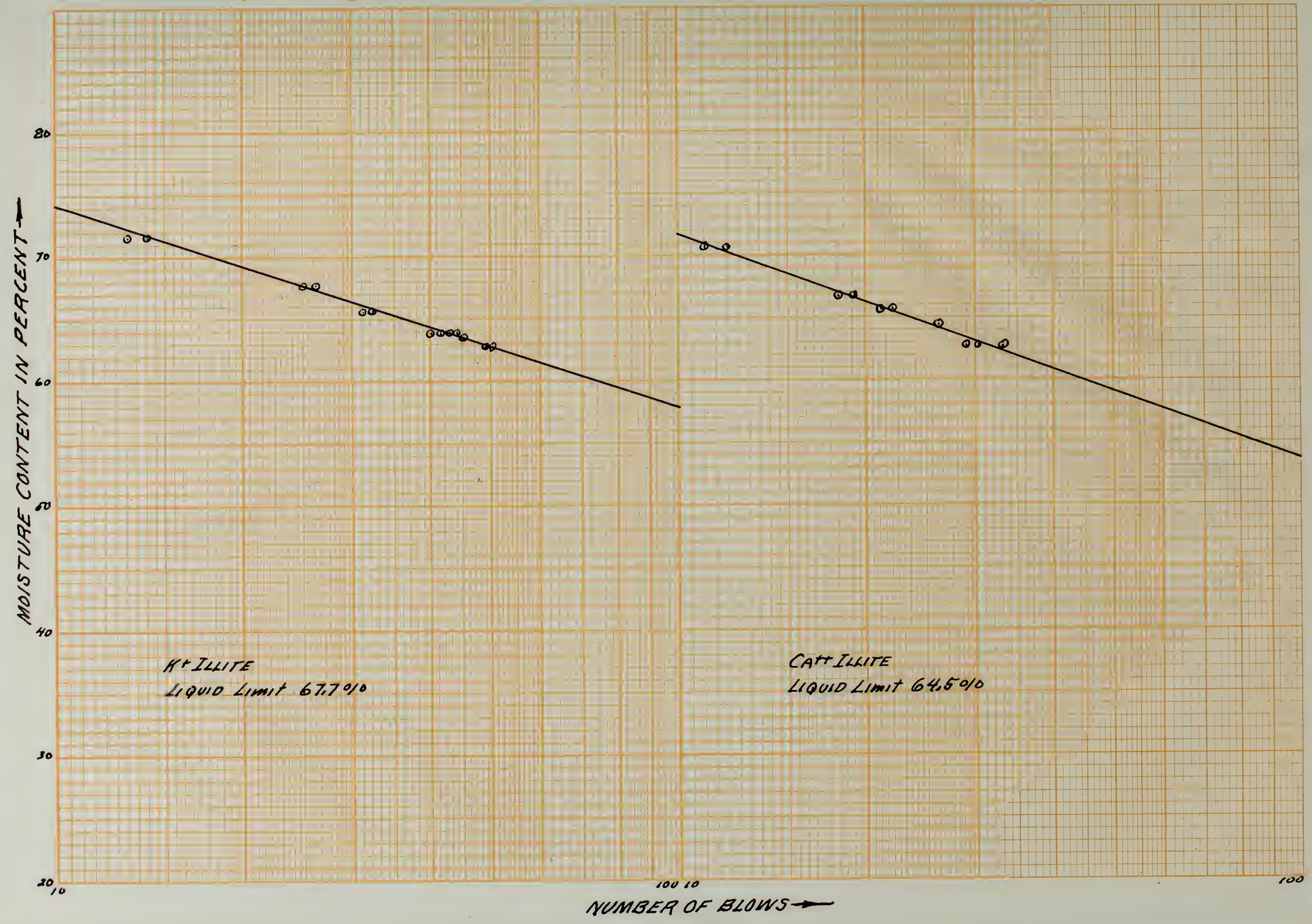

Na+ Kaolin
Batch #3
Liquid Limit 31.0%
H+ Kaolin
Batch #3
Liquid Limit 41.5%
NUMBER OF BLOWS →
MOISTURE CONTENT IN PERCENT →
0
10
20
30
40
50
10
100
1
2
3
4
5
6
7
8
9

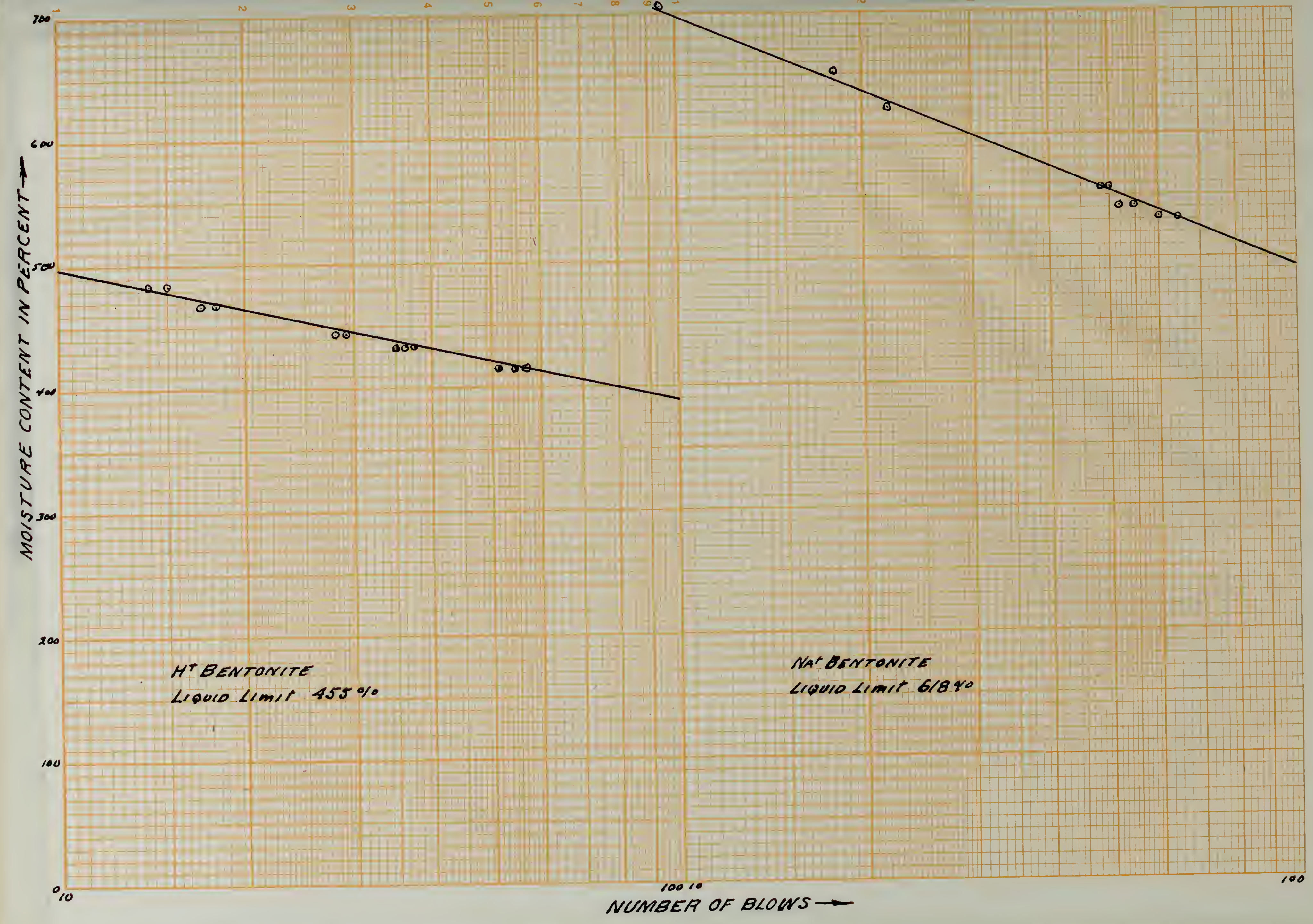

MOISTURE CONTENT IN PERCENT →
50
40
30
20
10
0
10
100 10
100
NUMBER OF BLOWS →
H+ KAOLIN
BATCH #3
LIQUID LIMIT 41.5%
NA+ KAOLIN
BATCH #3
LIQUID LIMIT 31.0%

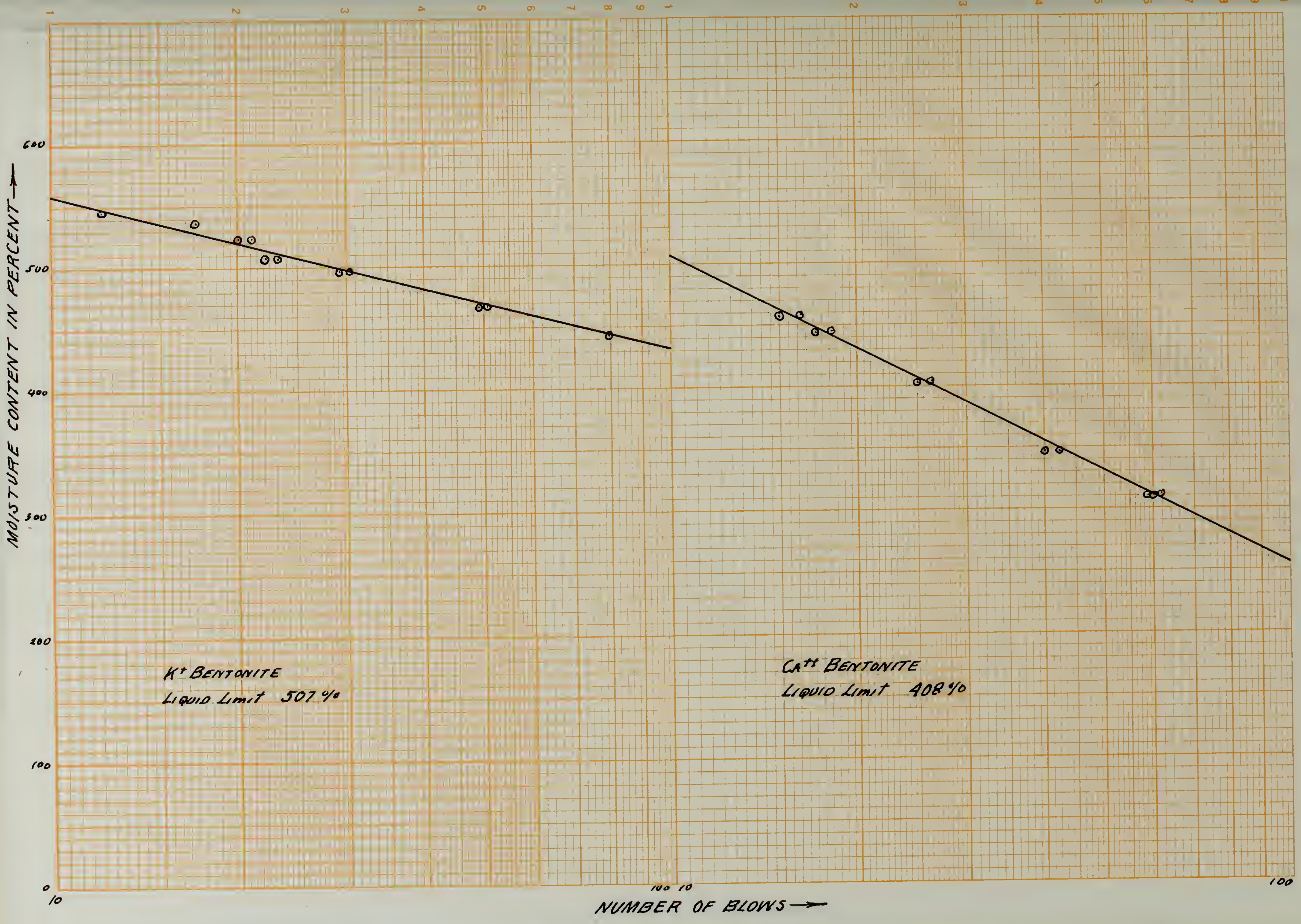

Ca^{++} KAOLIN
BATCH #3
LIQUID LIMIT 35.0%
K^{+} KAOLIN
BATCH #3
LIQUID LIMIT 31.0%
NUMBER OF BLOWS →
MOISTURE CONTENT IN PERCENT →
0
10
20
30
40
10
100 10
100


MOISTURE CONTENT IN PERCENT →
70
60
50
40
30
20
10
100 10
100
NUMBER OF BLOWS →
As Received Kaolin
Liquid Limit 43,8 %
As Received Illite
Liquid Limit 58.1%

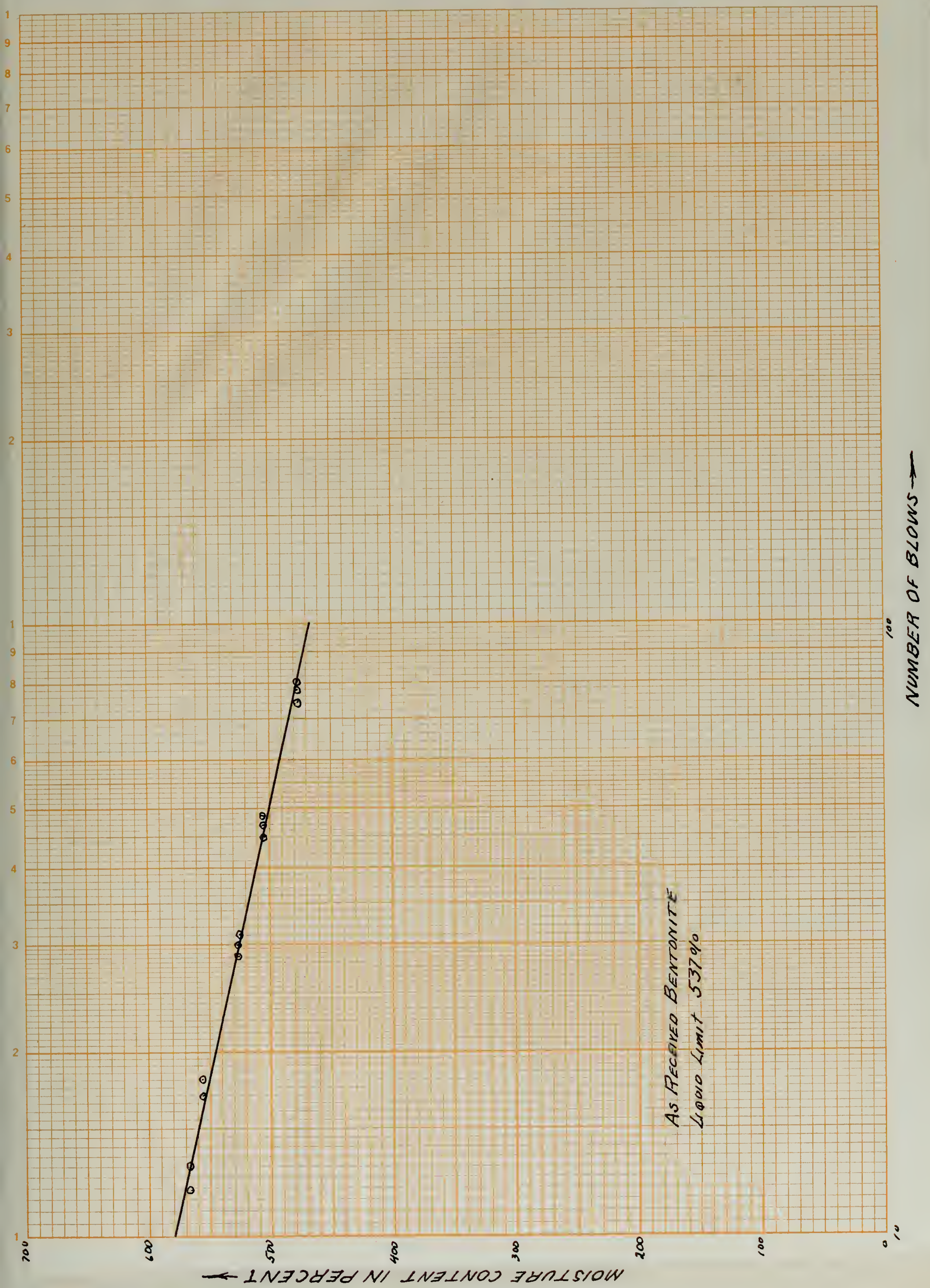

MOISTURE CONTENT IN PERCENT →
80
70
60
50
40
30
20
1
100 10
100
NUMBER OF BLOWS →
H+ ILLITE
LIQUID LIMIT 61.7 %
Na+ ILLITE
LIQUID LIMIT 65.3 %


80
70
60
50
40
30
20
10
100 10
100
MOISTURE CONTENT IN PERCENT→
NUMBER OF BLOWS→
K+ ILLITE
LIQUID LIMIT 67.7 0/0
Ca++ ILLITE
LIQUID LIMIT 64.5 0/0


MOISTURE CONTENT IN PERCENT
700
600
500
400
300
200
100
0
10
100 10
100
NUMBER OF BLOWS
H+ BENTONITE
LIQUID LIMIT 455 %
Na+ BENTONITE
LIQUID LIMIT 618 %



600
500
400
300
200
100
0
10
100 10
100
MOISTURE CONTENT IN PERCENT →
NUMBER OF BLOWS →
K+ BENTONITE
LIQUID LIMIT 507 %
CA++ BENTONITE
LIQUID LIMIT 408 %



As Received Bentonite
Liquid Limit 537%
NUMBER OF BLOWS →
← MOISTURE CONTENT IN PERCENT
700
600
500
400
300
200
100
0
10
100
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1

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Supplements

The information supplied in the supplements is the result of the work of the investigators named below, which was performed on the homoionic clays prepared by the authors of this thesis in the manner previously described. Further information is obtainable in the theses named below, which were submitted to the faculty of Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Master of Civil Engineering in May, 1951.

Supplement I - H. W. Merritt and E. E. White
"The Identification of Certain Clays
by Differential Thermal Analysis"

Supplement II - R. C. Williams and Keith H. Dearth
"The Identification and Investigation
of the Expansion Characteristics of
Clays by X-Ray Diffraction"

Supplement III - R.H.P. Dunn and G. A. Leighton
"An Investigation of the Base Exchange
Capacity of Certain Clay Minerals"

SUPPLEMENT 1

Investigation by Differential Thermal Analysis

Testing of kaolinite (batch #1) and bentonite in the differential thermal apparatus disclosed that both clays had definitely been affected by ionic substitution. The illite test results were not considered conclusive because of trouble with the thermocouples on these runs. Time did not permit retesting of this material. However, on the basis of the kaolinite and bentonite, results, it is logical to conclude that this material (illite) would also exhibit ionic substitution effects.

The following table gives the data obtained.

Clay	1st endothermic reaction Millivolt Equivalents	Temperature °C
H+ Kaolinite	.61	645
Na+ Kaolinite	.40	638
K+ Kaolinite	.54	645
Ca++ Kaolinite	.34	622
H+ Bentonite	.165	770
Na+ Bentonite	.145	770
K+ Bentonite	.160	767

The first endothermic reaction is a measure of the crystal lattice water which is distinct and separate from the interplaner water and water films as measured in a Casagrande tester. Therefore, there is no reason for the order of magnitude of these results being the same as the order of magnitude of the liquid limit.

SUPPLEMENT II

Investigation by X-ray Analysis

X-ray analysis of kaolinite (batch #1) showed no effects of ionic substitution. As this type of clay had a non-expanding lattice, this finding is in conformance with existing crystal lattice theory.

The illite bond clay gave the same x-ray patterns as an illite glanconite shale. These patterns had no inner rings, and hence it was impossible to measure variations in interplanar spacing regardless of the water content and cation attached.

The bentonite samples gave practically the same lattice spacing for the H+ and Ca++ clays. This spacing agrees with that of the H+ clay as reported by other investigators. The K+ and Na+ samples exhibited broad diffuse inner rings indicating a mixture of ions. It was concluded that the last two clays had the most displacement.

On the basis of these results, it is recommended that all samples be treated more than once to obtain purer ionic clays. If possible the illite should be separated from the illite glanconite shale, or if this is not feasible, a purer form of illite should be obtained. Test data obtained by X-ray analysis for the bentonites is calculated below.

Clay	Spacing of Innermost Ring in Angstroms	
	Dry	Hydrated
H+ Bentonite	13.79	20.30
Na+ Bentonite	13.49	
K+ Bentonite	13.89	
Ca++ Bentonite	13.62	19.03

SUPPLEMENT III

Spectrographic Analysis

Spectrographic analyses were conducted on the as received samples of kaolinite, illite, and bentonite, and on samples of H-kaolinite, H-illite, and H-bentonite. The purpose of this investigation was to determine how much exchange had taken place by the addition of the hydrochloric acid. For a complete explanation of method, see thesis by Lt. (jg) R.H.P. Dunn and Lt. (jg) G. A. Leighton, titled "An Investigation of the Base Exchange Capacity of Certain Clay Minerals" written at Rensselaer Polytechnic Institute, Troy, N. Y. May 1951.

The following results were obtained which show the amount of hydrogen ions adsorbed by each clay. These adsorbed hydrogen ions have displaced ions originally attached to the clay.

Clay	Exchange
Kaolinite	6.92 me of H ions/100 grams
Illite	25.10 me of H ions/100 grams
Bentonite	50.29 me of H ions/100 grams

A comparison of these values with the values obtained by potentiometric titration is given to show the completeness of exchange. Titration was made on the H-clay with .1 N NaOH.

Clay	Exchange	Percent Exchange
H-Kaolinite (Batch #1)	2.27 me/100 grams	32.9%
H-Illite	10.52 me/100 grams	42.0%
H-Bentonite	34.5 me/100 grams	68.7%

Bentonite is seen to have the most thorough replacement.

Thesis
E48
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An investigation of the effect of ionic substitution on the Atterberg plasticity constants of certain

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